Hummel (2)

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

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

August 1., 1992

MEMORANDUM

OFFICE OF PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: Mancozeb (014504) Update to Registration Standard Product and Residue Chemistry Chapter Updates [MRID Nos. 001607-80 to -81, 001645-10, 001648-79 to -80, 402583-01, 407646-01, 407680-01, 408697-01 to -17, 409133-01 to -06, 410700-01, 410916-01, 410917-01, 410918-01, 410920-01 to -07, 410932-01, 410952-01, 413431-01, 414432-01, 414838-01, 417318-01, 418315-01, 418448-01 to -02, 419011-02 to -03, 419761-01, 420369-01, 421559-01; CB Nos. 7466, 7959, 8514, 9250; DP Barcodes D159570, D164195, D167863, D173309]

FROM: Edward Zager, Chief
Chemistry Branch II-Reregistration Support
Health Effects Division (H7509C)

Edward Zager

TO: Lois Rossi, Chief
Terri Stowe, PM#71
Reregistration Branch
Special Review and Reregistration Division (H7508C)

Attached are the updates to the Product and Residue Chemistry Chapters for the Mancozeb Registration Standard. These updates were prepared by Dynamac Corporation under the supervision of CBRS, HED. They have undergone secondary review in the Branch and have been revised to reflect Agency policies.

Revised data requirement tables are included. If additional input is needed, please advise.

Attachment 1: Mancozeb Product Chemistry Registration Standard Update

Attachment 2: Mancozeb Residue Chemistry Registration Standard Update

Attachment 3: Confidential Appendix to Mancozeb Product Chemistry Registration Standard Update

cc w/ attachments: addressee, S. Hummel, Mancozeb Reg. Std. F.
cc w/o attachments: R.F., circu, S.F.
RDI:FBS:08/05/92:EZ:08/10/92
H7509C:CBII:SVH:svh:RM:810:CM#2:08/10/92

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DYNAMAC
CORPORATION

Final Report

MANCOZEB
Task 4: Product Chemistry Registration Standard Update

February 18, 1991

Contract No. 68-D8-0080

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
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Rockville, MD 20852

MANCOZEB

REGISTRATION STANDARD UPDATE

PRODUCT CHEMISTRY

TASK 4

INTRODUCTION

A Product Search Listing conducted 9/17/90 identifies a single registered manufacturing-use product (MP) for mancozeb, an 80% FI (EPA Reg. No. 707-102) produced by Rohm and Haas Company from a Rohm and Haas unregistered technical product (T). Unregistered Ts are also produced by E. I. Du Pont de Nemours & Company, and Pennwalt Corporation.

The Mancozeb Guidance Document dated 4/87 requires new generic and product-specific chemistry data for mancozeb, noting that although product chemistry data may have been submitted in the past, new requirements have been introduced, and previously submitted data must be updated. In response to the data requirements Rohm and Haas has submitted data (1987 and 1988; MRIDs 40373401, 40383301, 40605901, 40606001, 40620701, 40731401, 40898301, 40898302, and 41357901) for the 80% FI (EPA Reg. No. 707-102) and the unregistered T. Du Pont (1987 and 1988; MRIDs 40391801, 40517501, 40517502, and 40678201) and Pennwalt (1987 and 1988; MRIDs 40381201, 40381202, 40652201, 40765901, and 41056601) have submitted data for their unregistered Ts. These data have been reviewed by the Agency. Rohm and Haas has submitted additional data for the 80% FI and the unregistered T (DEB No. 7466; 1987; MRID 40373402 and 1989; MRIDs 41219401 and 41220401). These data are reviewed below for their adequacy in fulfilling outstanding data requirements.

Corresponding to each of the Topical Discussions listed below are the Guideline Reference Numbers from "Pesticide Assessment Guidelines - Subdivision D - Product Chemistry", referred to in Title 40 of the Code of Federal Regulations (40 CFR), Part 158, "Data Requirements for Registration", Subpart C, "Product Chemistry Data Requirements". These regulations and guidelines explain the minimum data that the Agency needs to adequately assess the product chemistry of mancozeb.

	Guidelines Reference No. from 40 CFR §158.155-190
Product Composition and Manufacture	61-(1-3)
Analysis and Certification of Product Ingredients .	62-(1-3)
Physical and Chemical Characteristics	63-(2-20)

SUMMARY

The following Mancozeb Product Chemistry data are required:

- For the Rohm and Haas 80% FI (EPA Reg. No. 707-102), additional data must be submitted pertaining to the starting materials and manufacturing process, discussion of the formation of impurities, preliminary analysis, certified limits, enforcement analytical methods, and the following physical/chemical properties: density, pH, and stability.

- For the Rohm and Haas unregistered T, additional data must be submitted pertaining to preliminary analysis.

- For the Du Pont unregistered T, additional data must be submitted pertaining to preliminary analysis, certified limits, enforcement analytical methods, and the following physical/chemical properties: solubility, octanol/water partition coefficient, stability, oxidizing/reducing action, flammability, explodability, storage stability, and corrosion characteristics.

- For the Pennwalt unregistered T, additional data must be submitted pertaining to preliminary analysis, certified limits, enforcement analytical methods, and the following physical/chemical properties: oxidizing/reducing action, flammability, explodability, storage stability, and corrosion characteristics.

PRODUCT IDENTITY AND COMPOSITION

61-1. Product Composition

The Mancozeb Guidance Document dated 4/87 requires generic and product-specific data concerning product composition.

In response to the Guidance Document, Rohm and Haas submitted data (1987; MRID 40373401) for the 80% FI (EPA Reg. No. 707-102) which were found to be identical to data reviewed for the Product Chemistry Science Chapter dated 9/10/86 (H. Fonouni, DEB Nos. 3228, 3229, 2937, dated 5/25/88). Although Fonouni noted that any deficiencies stated in the Science Chapter are still outstanding, data reviewed for product composition were found to be satisfactory. No additional data are required.

Data submitted by Rohm and Haas in response to the Guidance Document (1987; no MRID number) for the unregistered T were reviewed by G. Makhijani (DEB No. 4368, dated 11/9/88), who concluded that these data satisfy the requirements of 40 CFR §158.155 (Guideline Reference No. 61-1) regarding product

composition for the Rohm and Haas unregistered T. No additional data are required.

In response to the Guidance Document, Du Pont submitted data for the unregistered T which were reviewed by the Agency (1987; MRID 40391801, Fonouni, DEB No. 3046, dated 6/3/88; and 1987; MRID 40517502, Fonouni, DEB Nos. 3404, 3405, 3406, 3407, dated 6/10/88). These data were found to satisfy the requirements of 40 CFR §158.155 (Guideline Reference No. 61-1) regarding product composition for the Du Pont unregistered T. No additional data are required.

In response to the Guidance Document, Pennwalt submitted data (1987; MRID 40381201) for the unregistered T which were reviewed by H. Fonouni (DEB No. 2965, dated 6/8/88), and were found to satisfy the requirements of 40 CFR §158.155 (Guideline Reference No. 61-1) regarding product composition for the Pennwalt unregistered T. No additional data are required.

61-2. Starting Materials and Manufacturing Process

The Mancozeb Guidance Document dated 4/87 specifies generic and product-specific data requirements for mancozeb regarding starting materials and manufacturing/formulation processes.

In response to the Guidance Document, Rohm and Haas submitted data (1987; MRID 40373401) for the 80% FI (EPA Reg. No. 707-102) which were found to be identical to data reviewed for the Product Chemistry Science Chapter dated 9/10/86 (H. Fonouni, DEB Nos. 3228, 3229, 2937, dated 5/25/88). Fonouni stated that any deficiencies listed in the Science Chapter are still outstanding. Accordingly, the submitted data do not satisfy the requirements of 40 CFR §158.160-162 (Guideline Reference No. 61-2) regarding starting materials and the manufacturing process for the 80% FI (EPA Reg. No. 707-102) because insufficient information was provided regarding the relative amounts of beginning materials, equipment used to produce the product, reaction conditions, the duration of each step of the process, purification procedures, and quality control measures. Additional information is required.

Data submitted by Rohm and Haas for the unregistered T were reviewed by the Agency (1987; no MRID number, Makhijani, DEB No. 4368, dated 11/9/88; and 1987; MRID 40898301, Makhijani, DEB No. 4689, dated 12/16/88), and were found to satisfy the requirements of 40 CFR §158.160-162 (Guideline Reference No. 61-2) regarding starting materials and the manufacturing process for the Rohm and Haas unregistered T. No additional information is required.

In response to the Guidance Document, Du Pont submitted data for the unregistered T which were reviewed by the Agency (1987; MRID

40391801, Fonouni, DEB No. 3046, dated 6/3/88; and 1987; MRID 40517502, Fonouni, DEB Nos. 3404, 3405, 3406, 3407, dated 6/10/88). These data were found to satisfy the requirements of 40 CFR §158.160-162 (Guideline Reference No. 61-2) regarding starting materials and the manufacturing process for the Du Pont unregistered T. No additional information is required.

In response to the Guidance Document, Pennwalt submitted data (1987; MRID 40381201) for the unregistered T which were reviewed by H. Fonouni (DEB No. 2965, dated 6/8/88), and were found to satisfy the requirements of 40 CFR §158.160-162 (Guideline Reference No. 61-2) regarding starting materials and the manufacturing process for the Pennwalt unregistered T. No additional information is required.

61-3. Discussion of the Formation of Impurities

The Mancozeb Guidance Document dated 4/87 specifies generic and product-specific data requirements for mancozeb regarding discussion of formation of impurities.

In response to the Guidance Document, Rohm and Haas submitted data (1987; MRID 40373401) for the 80% FI (EPA Reg. No. 707-102) which were found to be identical to data reviewed for the Product Chemistry Science Chapter dated 9/10/86 (H. Fonouni, DEB Nos. 3228, 3229, 2937, dated 5/25/88). Fonouni noted that any deficiencies stated in the Science Chapter are still outstanding. Accordingly, the submitted data do not satisfy the requirements of 40 CFR §158.167 (Guideline Reference No. 61-3) regarding discussion of formation of impurities in the 80% FI (EPA Reg. No. 707-102) because the submission does not include a complete theoretical discussion of potential impurities based on post-production reactions between components of the product or its packaging. Additional information is required.

Data submitted by Rohm and Haas for the unregistered T (1987; no MRID number) were reviewed by G. Makhijani (DEB No. 4368, dated 11/9/88), and were found to satisfy the requirements of 40 CFR §158.167 (Guideline Reference No. 61-3) regarding discussion of formation of impurities for the Rohm and Haas unregistered T. No additional information is required.

In response to the Guidance Document, Du Pont submitted data for the unregistered T which were reviewed by the Agency (1987; MRID 40391801, Fonouni, DEB No. 3046, dated 6/3/88; and 1987; MRID 40517502, Fonouni, DEB Nos. 3404, 3405, 3406, 3407, dated 6/10/88). These data were found to satisfy the requirements of 40 CFR §158.167 (Guideline Reference No. 61-3) regarding discussion formation of impurities for the Du Pont unregistered T. No additional information is required.

In response to the Guidance Document, Pennwalt submitted data (1987; MRID 40381201) for the unregistered T which were reviewed by H. Fonouni (DEB No. 2965, dated 6/8/88), and were found to satisfy the requirements of 40 CFR §158.167 (Guideline Reference No. 61-3) regarding discussion of formation of impurities for the Pennwalt unregistered T. No additional information is required.

ANALYSIS AND CERTIFICATION OF PRODUCT INGREDIENTS

62-1. Preliminary Analysis

The Mancozeb Guidance Document dated 4/87 specifies generic and product-specific data requirements for mancozeb regarding preliminary analysis.

In response to the Guidance Document, Rohm and Haas submitted data for the 80% FI (EPA Reg. No. 707-102) and the unregistered T (1988; MRIDs 40620701 and 40606001, respectively) which were reviewed by H. Fonouni (DEB Nos. 3835, 3839, 3889, dated 7/1/88). Fonouni concluded that the data do not satisfy the requirements of 40 CFR §158.170 (Guideline Reference No. 62-1) because data were not submitted for two impurities which are reportedly present at a level >0.1% of the product (MRID 00147940), the nitrosamine method used was not sufficiently accurate, and because compositional analysis was not provided for the product, including its impurities, using method(s) which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants. Fonouni noted that all analytical data submitted must be validated.

New data (1989; MRID 41220401 and 41219401) submitted by Rohm and Haas in response to Fonouni's review are presented in Confidential Appendix A, and do not satisfy the requirements of 40 CFR §158.170 (Guideline Reference No. 62-1) for the 80% FI (EPA Reg. No. 707-102) and the unregistered T because the requirement for compositional analysis using method(s) which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants, including other EBDC fungicides (see Hummel, DEB No. 2725, dated 4/21/88), has not been satisfied. Additional data are required.

In response to the Guidance Document, Du Pont submitted data (1988; 40678201) for the unregistered T which were reviewed by H. Fonouni (DEB No. 4073, dated 8/15/88). Fonouni concluded that the data do not satisfy the requirements of 40 CFR §158.170 (Guideline Reference No. 62-1) regarding preliminary analysis for the Du Pont unregistered T because compositional analysis must be provided for the product using methods which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants. In addition, data were not submitted for two impurities. Additional data are required.

In response to the Guidance Document, Pennwalt submitted data (1988; MRID 40652201) for the unregistered T which were reviewed by H. Fonouni (DEB No. 4020, dated 7/28/88). He concluded that the data do not satisfy the requirements of 40 CFR §158.170 (Guideline Reference No. 62-1) regarding preliminary analysis for the Pennwalt unregistered T because compositional analysis must be provided for the unregistered technical using methods which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants. Fonouni noted that validation data must be provided for the analytical methods used. Additional data are required.

62-2. Certified Limits

The Mancozeb Guidance Document dated 4/87 specifies generic and product-specific data requirements for mancozeb regarding certification of ingredient limits.

In response to the Guidance Document, Rohm and Haas submitted data (1988; MRIDs 40605901 and 40620701) for the 80% FI (EPA Reg. No. 707-102) which were reviewed by H. Fonouni (DEB Nos. 3835, 3839, 3889, dated 7/1/88). He concluded that the submitted data do not satisfy the requirements of 40 CFR §158.175 (Guideline Reference No. 61-2) regarding certified limits for the Rohm and Haas 80% FI (EPA Reg. No. 707-102) because certified limits must be established for the product, including its impurities, using method(s) which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants. In addition, upper certified limits are required for two additional impurities reportedly present at a level >0.1% of the product (MRID 00147940), and for nitrosamines. Fonouni also notes that an upper certified limit for an inert ingredient listed on the registrant's CSF dated 7/2/87 is not in agreement with the value submitted by the registrant in MRID 40620701.

In response to Fonouni's review Rohm and Haas (1989; MRID 41220401) states that the previously submitted certified limits are still appropriate based on: (i) analysis of the 80% FI (EPA Reg. No. 707-102) by a method capable of distinguishing between mancozeb per se and other potential carbon disulfide-producing contaminants (see Confidential Appendix B); (ii) the absence of any evidence of additional impurities at >0.1%; and (iii) further analysis for nitrosamines using an improved method (see Confidential Appendix A). This statement does not satisfy the requirements of 40 CFR §158.175 (Guideline Reference No. 61-2) regarding certified limits for the Rohm and Haas 80% FI (EPA Reg. No. 707-102) because the requirement for certified limits based on analysis by a method which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants, including other EBDC fungicides (see Hummel, DEB No. 2725, dated

4/21/88), has not been satisfied. In addition, the upper certified limit for the inert ingredient mentioned in Fonouni's review has not been corrected on the CSF (EPA Form 8570-4 Rev. 2-85). Additional data are required.

Certified limits are not required for the Rohm and Haas unregistered T because it is never isolated from the manufacturing process for the 80% FI (EPA Reg. No. 707-102).

In response to the Guidance Document, Du Pont submitted data (1988; MRID 40678201) for the unregistered T which were reviewed by H. Fonouni (DEB No. 4073, dated 8/15/88). He concluded that the data do not satisfy the requirements of 40 CFR §158.175 (Guideline Reference No. 62-2) regarding certified limits for the Du Pont unregistered T because certified limits must be established for products containing the unregistered technical using analytical method(s) which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants. In addition, upper certified limits are required for three impurities of toxicological concern reportedly present at a level ≥0.1% of the product. Additional data are required.

In response to the Guidance Document, Pennwalt submitted data for the unregistered T which were reviewed by the Agency (1987; MRID 40381201, Fonouni, DEB No. 2965, dated 6/8/88; 1988; MRID 40652201, Fonouni, DEB No. 4020, dated 7/28/88; Pennwalt letter dated 6/3/88, Fonouni, DEB No. 4270, dated 8/25/88; and 1988; no MRID number, Makhijani, DEB No. 4747, dated 1/17/89). These data do not satisfy the requirements of 40 CFR §158.175 (Guideline Reference Nos. 62-2) because certified limits must be established for the unregistered technical using method(s) which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants. In addition, certified limits have not been established for nitrosamines using a validated method. Additional data are required.

62-3. Enforcement Analytical Methods

The Mancozeb Guidance Document dated 4/87 specifies generic and product-specific data requirements for mancozeb regarding analytical methods to verify certified limits. Although the Guidance Document states that an analytical method is required which differentiates between mancozeb per se and interfering (CS_2-liberating) impurities which may be present, the Agency further requires (Hummel, DEB No. 2725, dated 4/21/88) that the enforcement method be capable of distinguishing between/among the different EBDC fungicides.

In response to the Guidance Document, Rohm and Haas submitted data for the 80% FI (EPA Reg. No. 707-102) which were reviewed by the Agency (1988; MRIDs 40605901 and 40620701, Fonouni, DEB Nos.

3835, 3839, 3889, dated 7/1/88; and 1987; MRID 41357901, Makhijani, DEB No. 6394, dated 4/17/90). These data do not satisfy the requirements of 40 CFR §158.180 (Guideline Reference No. 62-3) regarding enforcement analytical methods for the Rohm and Haas 80% FI (EPA Reg. No. 707-102) because methodology capable of distinguishing mancozeb per se from other carbon disulfide-producing contaminants must be provided. In addition, validation data are required for two methods used to determine impurities.

In response to the Agency review, Rohm and Haas submitted (1989; 41220401) revisions of methods originally reviewed by H. Fonouni (DEB Nos. 3835, 3839, 3889, dated 7/1/88). Details are presented in Confidential Appendix B. These data do not satisfy the requirements of 40 CFR §158.180 (Guideline Reference No. 62-3) regarding enforcement analytical methods for the Rohm and Haas 80% FI (EPA Reg. No. 707-102) because the requirement for method(s) which would distinguish mancozeb per se from other potential carbon disulfide-producing contaminants, including other EBDC fungicides (see Hummel, DEB No. 2725, dated 4/21/88), has not been satisfied. Additional data are required.

Enforcement analytical methods are not required for the Rohm and Haas unregistered T because it is never isolated from the manufacturing process for the 80% FI (EPA Reg. No. 707-102).

In response to the Guidance Document, Du Pont submitted data for the unregistered T which were reviewed by the Agency (1987; MRID 40517501, Fonouni, DEB No. 3404, 3405, 3406, 3407 dated 6/10/88; and 1988; MRID 40678201, Fonouni, DEB No. 4073, dated 8/15/88). These data do not satisfy the requirements of 40 CFR §158.180 (Guideline Reference No 62-3) regarding enforcement analytical methods for the Du Pont unregistered T because analytical method(s) capable of distinguishing mancozeb per se from other potential carbon disulfide-producing contaminants must be provided. In addition, validation data, including recovery, must be provided for a method used to determine an impurity. Additional data are required.

In response to the Guidance Document, Pennwalt submitted data (1988; MRID 40652201) for the unregistered T which were reviewed by H. Fonouni (DEB No. 4020, dated 7/28/88). He concluded that the data do not satisfy the requirements of 40 CFR §158.180 (Guideline Reference No 62-3) regarding enforcement analytical methods for the Pennwalt unregistered T because analytical method(s) capable of distinguishing mancozeb per se from other potential carbon disulfide-producing contaminants must be provided. In addition, validation data indicating accuracy and precision must be provided for the submitted methods. Additional data are required.

PHYSICAL AND CHEMICAL CHARACTERISTICS

The Mancozeb Guidance Document dated 4/87 specifies generic and product-specific data requirements for all physical and chemical characteristics pertinent to the technical grade of the active ingredient (TGAI) and manufacturing-use products (MPs).

In response to the Guidance Document, Rohm and Haas submitted data (1987; MRID 40373402) for the 80% FI (EPA Reg. No. 707-102) which are summarized in Table 1. These data satisfy the requirements of 40 CFR §158.190 (Guideline Reference Nos. 63-2 through 63-20) regarding most physical and chemical characteristics of the 80% FI (EPA Reg. No. 707-102). Data requirements remain outstanding for the following physical/chemical characteristics: bulk density (Guideline Reference No. 63-7) because temperature, units, and the method used were not specified; pH (Guideline Reference No. 63-12) because the temperature was not specified; and stability (Guideline Reference No. 63-13) because information was not provided pertaining to the stability of the product when exposed to metal and metal ions, elevated temperatures, and sunlight. A subsequent submission (1988; MRID 40731401) pertaining to stability (Guideline Reference No. 63-13) and storage stability (Guideline Reference No. 63-17) was reviewed by H. Fonouni (DEB No. 4205, dated 8/25/88) who concluded that data requirements for stability remain outstanding. Additional data are required.

Data submitted for the Rohm and Haas unregistered T were reviewed by the Agency (1988; no MRID number, Makhijani, DEB No. 4368, dated 11/9/88; 1987; MRID 40898302, Makhijani, DEB No. 4689, dated 12/16/88; 1987; MRID 40383301, Anthony, DEB No. 4644, dated 3/3/89; and 1987; MRID 41357901, Makhijani, DEB No. 6394, dated 4/17/90). These data were found to satisfy the requirements of 40 CFR §158.190 (Guideline Reference Nos. 63-2 through 63-12) for the TGAI of the Rohm and Haas unregistered T. In a separate review, Makhijani (DEB No. 4743, dated 1/17/89) concluded that data pertaining to stability were not required for the Rohm and Haas unregistered T because it is never isolated from the manufacturing process for the 80% FI (EPA Reg. No. 707-102). For this reason physical/chemical characteristics pertaining to manufacturing-use products, Guideline Reference Nos. 63-14 through 63-20, are not required for the unregistered T. No additional data are required.

In response to the Guidance Document, Du Pont submitted data for the unregistered T which were reviewed by the Agency (1987; MRID 40391801, Fonouni, DEB No. 3046, dated 6/3/88; 1987; MRID 40517502, Fonouni, DEB Nos. 3404, 3405, 3406, and 3407, dated 6/10/88; and 1988; no MRID number, Makhijani, DEB No. 4750, dated 1/24/89). These data satisfy the requirements of 40 CFR §158.190 (Guideline Reference Nos. 63-2 through 63-13), except for solubility, octanol/water partition coefficient, and stability

(Guideline Reference No. 63-8, 63-11, and 63-13, respectively) for the TGAI of the Du Pont unregistered T. We note that data requirements also remain outstanding for oxidizing or reducing action, flammability, explodability, storage stability, and corrosion characteristics (Guideline Reference Nos. 63-14 through 63-20) for the Du Pont unregistered T as an MP. Additional data are required.

In response to the Guidance Document, Pennwalt submitted data for the unregistered T which were reviewed by the Agency (1987; MRID 40381202, Fonouni, DEB No. 2965, dated 6/8/88; 1988; MRID 40765901, Fonouni, DEB No. 4270, dated 8/25/88; and 1988; MRID 41056601, Makhijani, DEB No. 5267, dated 6/20/89). These data satisfy the requirements of 40 CFR §158.190 (Guideline Reference Nos. 63-2 through 63-13) for the TGAI of the Pennwalt unregistered T. We note that data requirements remain outstanding for oxidizing or reducing action, flammability, explodability, storage stability, and corrosion characteristics (Guideline Reference Nos. 63-14 through 63-20) for the Pennwalt unregistered T as an MP. Additional data are required.

Table 1. Physical and chemical properties of the Rohm and Haas 80% FI (EPA Reg. No. 707-102). Data are from MRID 40373402.

Guidelines Reference No., 40 CFR §158.190; Name of Property		Description [Method]
63-2.	Color	light yellow
63-3.	Physical state	free flowing powder
63-4.	Odor	slight hydrogen sulfide-like odor
63-5.	Melting point	decomposes at 150 C
63-6.	Boiling point	not applicable
63-7.	Density, bulk density, or specific gravity	loose - 0.43, packed - 0.48

(Continued.)

Table 1. (Continued.)

Guidelines Reference No., 40 CFR §158.190; Name of Property	Description [Method]
63-8. Solubility	essentially insoluble in most organic solvents; water solubility - 5.0×10^{-5} moles/L 13.6 μg/ml [UV absorption of filtered mancozeb slurry]
63-9. Vapor pressure	negligible
63-10. Dissociation constant	not applicable
63-11. Octanol/water partition coefficient	K_{ow} = 1.8 ± 0.1; 0.1 g product vs 20 ml octanol vs 20 ml water
63-12. pH	6.5 - 7.5, aqueous slurry
63-13. Stability	decomposed by water under acidic conditions
63-14. Oxidizing or reducing action	under normal conditions does not function as an oxidizing or reducing agent
63-15. Flammability	138 C; tag open cup
63-16. Explodability	will not propagate a spontaneous explosion
63-17. Storage stability	8% loss of active ingredient during 24 months storage of unopened pack-out bags warehoused at 12 C; no weight loss or measurable increase in degradation products
63-18. Viscosity	not applicable
63-19. Miscibility	not applicable
63-20. Corrosiveness	non-corrosive; can be stored in metal and/or plastic containers

MASTER RECORD IDENTIFICATION NUMBERS

MRID documents containing data which have been reviewed by the Agency are designated in shaded blocks in the following bibliographic listing of Product Chemistry Citations (used). A summary of the subject memoranda and their associated MRID documents is presented below.

AGENCY MEMORANDA

DEB No. 2725
Subject: Rohm and Haas Response to Registration Standard
Rohm and Haas letter of 7/2/87 (90-day response)
Rohm and Haas letter of 7/6/87 (Response to Product Chemistry Data Gaps)
Rohm and Haas letter of 7/6/87 (Response to Residue/Metabolism Data Gaps)
From: S.V. Hummel
To: L. Rossi
Dated: 4/21/88
MRID(s) 40258301

DEB No. 2965
Subject: Product Chemistry Data Submitted in Response to eh Mancozeb Registration Standard
From: H. Fonouni
To: L. Rossi and A. Rispin
Dated: 6/8/88
MRID(s): 40381201, 40381202

DEB No. 3046
Subject: Product Chemistry Data Submitted in Response to the Mancozeb Registration Standard
From: H. Fonouni
To: L. Rossi
Dated: 6/3/88
MRID(s): 40391801

DEB Nos. 3228, 3229, 2937
Subject: Mancozeb Registration Standard, Product Chemistry Data Submitted for Dithane® M-45, Concentrate and Agricultural Fungicide
From: H. Fonouni
To: L. Rossi
Dated: 5/25/88
MRID(s): 40373401 (reviewed), 40373402 (not reviewed)

DEB Nos. 3404, 3405, 3406, 3407
Subject: Data Call In for Products Containing Mancozeb - Mancozeb Registration Standard
From: H. Fonouni
To: L. Rossi

Dated: 6/10/88
MRID(s): 40517501, 40517502

DEB Nos. 3835, 3839, 3889
Subject: Mancozeb Registration Standard
From: H. Fonouni
To: L. Rossi
Dated: 7/1/88
MRID(s): 40605901, 40606001, 40620701

DEB No. 4020
Subject: Pennwalt Corporation's Response to the Mancozeb Registration Standard
From: H. Fonouni
To: L. Rossi
Dated: 7/28/88
MRID(s): 40652201

DEB No. 4073
Subject: E.I. du Pont de Nemours & Company, Inc. Response to the Mancozeb Registration Standard
From: H. Fonouni
To: L. Rossi
Dated: 8/15/88
MRID(s): 40678201

DEB No. 4205
Subject: Response to Mancozeb Registration Standard, Rohm and Haas Company
From: H. Fonouni
To: L. Rossi
Dated: 8/25/88
MRID(s): 40731401

DEB No. 4270
Subject: Response to the Mancozeb Registration Standard, Pennwalt Corporation
From: H. Fonouni
To: L. Rossi
Dated: 8/25/88
MRID(s): 40765901

DEB No. 4368
Subject: Mancozeb Unregistered Technical - Rohm & Haas Company - Product Chemistry Data Dated August 30, 1988
From: G. Makhijani
To: L. Rossi and R. Engler
Dated: 11/9/88
MRID(s): No MRID Number Assigned

DEB No. 4644
Subject: Mancozeb [DITHANE®-45M]: Product Chemistry, Series 63 data for the Rohm & Haas "Unregistered Technical"
From: W. Anthony
To: L. Rossi/S. Lewis
Dated: 3/3/89
MRID(s): 40383301

DEB No. 4689
Subject: Mancozeb - Unregistered Technical - Rohm & Haas Company - Product Chemistry Data Dated November 18, 1988
From: G. Makhijani
To: L. Rossi and R. Engler
Dated: 12/16/88
MRID(s): 40898301, 40898302

DEB No. 4743
Subject: Mancozeb - Unregistered Technical - Rohm and Haas Company - Product Chemistry Data Dated December 2, 1988
From: G. Makhijani
To: L. Rossi and R. Engler
Dated: 1/17/89
MRID(s): No MRID Number Assigned

DEB No. 4747
Subject: Mancozeb - Unregistered Technical - Pennwalt Corporation - Product Chemistry Data, Dated December 5, 1988
From: G. Makhijani
To: L. Rossi and R. Engler
Dated: 1/17/89
MRID(s): No MRID Number Assigned

DEB No. 4750
Subject: Mancozeb - Unregistered Technical and Manufacturing Use Products - E.I. DuPont de Nemours and Company, Inc. - Product Chemistry Data Dated December 2, 1988
From: G. Makhijani
To: L. Rossi and R. Engler
Dated: 1/24/89
MRID(s): No MRID Number Assigned

DEB No. 5267
Subject: Mancozeb Registration Standard Follow-up - Product Chemistry - Pennwalt Corporation
From: G. Makhijani
To: S. Lewis/C. Grable and R. Engler
Dated: 6/29/89
MRID(s): 41056601

DEB No. 6394
Subject: Mancozeb - Unregistered Technical - Response of E.I. du Pont de Nemours and Company, Inc. to the Product Chemistry Chapter - Reregistration Guidance Document
From: G. Makhijani
To: J.B. Baker
Dated: 4/17/90
MRID(s): 41357901

Product Chemistry Citations (used):

40373401 Johnson, R. (1987) Product Identity and Composition: Dithane M-45: Report No. RWN-87-135A. Unpublished compilation prepared by Rohm and Haas Co. 31 p.

40373402 Johnson, R. (1987) Physical and Chemical Characteristics: Dithane M-45: Report No. RWN-87-135C. Unpublished compilation prepared by Rohm and Haas Co. 17 p.

40381201 Kool, P. (1987) Product Chemistry for Mancozeb Technical: Study ID No. MCZPC-61-87. Unpublished study prepared by Pennwalt Holland--Agchem. 5 p.

40381202 Kool, P. (1987) Product Chemistry for Mancozeb Technical: Study ID No. MCZPC-63-87. Unpublished study prepared by Pennwalt Holland--Agchem. 5 p.

40383301 Johnson, R. (1987) Product Chemistry for Mancozeb Unregistered "Technical": Laboratory Project ID No. RWN-82-133A. Unpublished study prepared by Rohm and Haas Co. 11 p.

40391601 Keeler, D. (1987) Product Chemistry for Du Pont Mancozeb Composition: Laboratory Project ID 7331. A (ES). Unpublished study prepared by E. I. Du Pont de Nemours and Co., Inc. 13 p.

40517501 Waegbe, T. (1987) Maneb and Mancozeb Assays: CS2 Evolution Method: M16. 0282(R). Unpublished study prepared by E. I. du Pont de.Nemours an Co., Inc. 20 p.

40517502 Keeler, D. (1987) Product Chemistry for Du Pont Mancozeb Composition from Secondary Manufacturing Source: Proj. ID 7331. B. Unpublished study prepared by E. I. du Pont de Nemours and Co., Inc. 21 p.

40605901 Hafer, J.; Nichols, R. (1988) Product Chemistry Section for Dithane M-45 Concentrate: Project I. D. No. RWN-88-048. Unpublished study prepared by Rohm and Haas Co. 19 p.

40606001 Hafer, J.; Nichols, R. (1988) Product Chemistry Section for Mancozeb Unregistered Dry Solid "Technical": Project I. D. No. RWN-88-049. Unpublished study prepared by Rohm and Haas Co. 11 p.

40620701 Hafer, J.; Nichols, R. (1988) Product Chemistry Section for Dithane M-45 Concentrate: Project I. D. No. RWN-88-037. Unpublished compilation prepared by Rohm and Haas Co. in cooperation with Galbraith Laboratories, Inc. 134 p.

40652201 Kool, P. (1988) Mancozeb Technical: Product Chemistry: Project ID: PW-115. Unpublished study prepared by Pennwalt Holland B. V. 41 p.

40678201 Waeghe, T. (1988) Product Chemistry for DuPont Mancozeb Composition from Primary and Secondary Manufacturing Sources: Analysis and Certification of Product Ingredients: Project ID: 7331. C. Unpublished study prepared by E. I. du Pont de Nemours and Co., Inc. 90 p.

40731401 Hafer, J.; Nichols, R. (1988) Product Chemistry Section for Dithane M-45 Concentrate: Project I. D. No. RWN-88-076. Unpublished study prepared by Rohm and Haas Co. 6 p.

40765901 Kool, P. (1988) Mancozeb Technical: Product Stability: Laboratory Project ID: PW-116. Unpublished compilation prepared by Penn-walt Holland B. V. 8 p.

40898301 Johnson, R. (1987) Product Chemistry for Mancozeb Unregistered "Technical": Laboratory Project ID No. RWN-87-133. Unpublished compilation prepared by Rohm and Haas Co. 9 p.

40898302 Venable, S. (1983) Dithane M-45 Solubility Study: Project ID No. : 13-83-96. Unpublished study prepared by Rohm and Haas Co. 8 p.

41056601 Kool, P. (1988) Mancozeb Technical: Product Stability: Proj. ID PW-123. Unpublished study prepared by Penwalt Holland B. V. 8 p.

41219401 Nichols, R. (1989) Addendum to Product Chemistry Section for Mancozeb Unregistered Technical: Proj. No. CPR-89-262. Unpublished study prepared by Rohm and Haas Co. 20 p.

41220401 Nichols, R. (1989) Addendum to Dithane M-45 Concentrate Product Chemistry (RWN-88-037, MRID Number 40620701): Project No. CPR-89-249. Unpublished study prepared by Rohm and Haas Co. 123 p.

41357901 Schweitzer, M. (1987) Water Solubility of Mancozeb: Lab Project Number: 31C/87/36. Unpublished study prepared by Rohm and Haas Co. 70 p.

Product Chemistry Citations (not used):
[These MRIDs contain duplicate data or data pertaining to end-use products]

40149001 Patel, C. (1987) RH-0611 WP Fungicide--Product Identity and Composition: Lab Project ID: 87-23. Unpublished compilation prepared by Rohm and Haas Co. 4 p.

40149002 Patel, C. (1987) RH-0611 WP Fungicide--Analysis and Certification of Product Ingredients: Lab Project No. : 87-23. Unpublished compilation prepared by Rohm and Haas Co. 4 p.

40388701 Brown, R. (1987) Ridomil MZ77 Fungicide: Product Chemistry Data: Study No. PC-87-017. Unpublished compilation prepared by Ciba-Geigy Corp. 113 p.

40625601 Kool, P. (1988) Penncozeb 75DF: Product Chemistry: Project ID: PW-103. Unpublished study prepared by Pennwalt Holland B. V. 11 p.

40625602 Kool, P. (1988) Penncozeb 75DF: Product Chemistry: Project ID: PW-105. Unpublished study prepared by Pennwalt Holland B. V. 6 p.

40676801 Kool, P. (1988) Penncozeb 75DF: Product Chemistry: Proj. ID PW-103A. Unpublished supplemental study prepared by Penwalt Holland. B. V. 9 p.

40676802 Kool, P. (1988) Penncozeb 75DF: Product Chemistry: Proj. ID PW-104A. Unpublished study prepared by Pennwalt Holland, B. V. 8 p.

40941301 Hobson, J. (1988) Manex II: Product Chemistry. Unpublished compilation prepared by Griffin Corp. 125 p.

40957401 Harvey, J. (1988) Penncozeb 4F: Product Chemistry: Project ID: PW-106. Unpublished study prepared by Pennwalt Corp. 5 p.

40957402 Harvey, J. (1988) Penncozeb 4F: Product Chemistry: Project ID: PW-107. Unpublished study prepared by Pennwalt Corp. 6 p.

40957403 Harvey, J. (1988) Penncozeb 4F: Product Chemistry: Project ID: PW-108. Unpublished study prepared by Pennwalt Corp. 6 p.

TABLE A. GENERIC DATA REQUIREMENTS FOR THE MANCOZEB TECHNICAL GRADE OF THE ACTIVE INGREDIENT.[1]

Data Requirement	Test Substance[2]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[3]	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
40 CFR §158.155-190 Product Chemistry				
Product Composition				
61-2. Beginning Materials and Production Process	TGAI	Yes	40381201 40391801 40517502 40898301	No
61-3. Formation of Impurities	TGAI	Yes	40381201 40391801 40517502	No
Analysis and Certification of Product Ingredients				
62-1. Preliminary Analysis	TGAI	Partially	40606001 40652201 40678201 41219401	Yes[4]
Physical and Chemical Characteristics[5]				
63-2. Color	TGAI	Yes	40381202 40383301 40391801 40517502	No
63-3. Physical State	TGAI	Yes	40381202 40383301 40391801 40517502	No
63-4. Odor	TGAI	Yes	40381202 40383301 40391801 40517502	No
63-5. Melting Point	TGAI	Yes	40381202 40383301 40391801 40517502	No
63-6. Boiling Point	TGAI	N/A	N/A	No
63-7. Density, Bulk Density, or Specific Gravity	TGAI	Yes	40381202 40383301 40391801 40517502	No
63-8. Solubility	TGAI or PAI	Partially	40381202 40383301 40391801 40517502 40898302	Yes[6]
63-9. Vapor Pressure	TGAI or PAI	Yes	40381202 40383301 40391801 40517502	No

(Continued, footnotes follow)

TABLE A. (Continued).

Data Requirement	Test Substance	Does EPA have data to satisfy this requirement?	Bibliographic Citation	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
63-10. Dissociation Constant	TGAI or PAI	Yes	40381202 40383301 40391801 40517502	No
63-11. Octanol/Water Partitioning Coefficient	PAI	Partially	40381202 40383301 40391801 40517502	Yes[7]
63-12. pH	TGAI	Yes	40381202 40383301 40391801 40517502	No
63-13. Stability	TGAI	Partially	40381202 40383301 40391801 40517502 40765901 41056601	Yes[8]
Other Requirements:				
64-1. Submittal of Samples	N/A	N/A	N/A	No

1. Data requirements pertain to the unregistered Ts produced by Rohm and Haas, Du Pont, and Pennwalt. Additional data requirements are listed in the following Table B, "Product Specific Data Requirements for Mancozeb Manufacturing-Use Products".

2. Test substance: PAI = purified active ingredient; TGAI = technical grade of the active ingredient; MP = manufacturing-use product.

3. Underlining indicates documents that have been reviewed in this Update Document.

4. Rohm and Haas, Du Pont, and Pennwalt have responded to data requirements for their unregistered Ts; however compositional analysis must be provided for five or more representative samples of the unregistered technicals, including their impurities, using methods which distinguish mancozeb per se from other potential carbon disulfide producing contaminants. Complete and detailed descriptions of the methods used for sample analysis must be submitted, including statements of their precision and accuracy.

TABLE A. (Continued).

5. As required by 40 CFR §158.190 and more fully described in the Pesticide Assessment Guidelines, Subdivision D, Guidelines Reference Nos. 63-2 through 63-13, data must be submitted on physicochemical characteristics (color, physical state, odor, melting point, boiling point, specific gravity, solubility, vapor pressure, dissociation constant, octanol/water partition coefficient, pH, and stability). There are additional data requirements listed in Table B pertaining to physicochemical characteristics of those technical products which are also manufacturing use products.

6. Du Pont has responded to data requirements for its unregistered T; however additional data are required pertaining to the solubility of the technical in distilled water and representative polar and non-polar organic solvents at 20 or 25 C. Rohm and Haas and Pennwalt have responded for their unregistered Ts, and data are adequate.

7. Du Pont has responded to data requirements for its unregistered T; however data on octanol/water partition coefficient are required if the technical chemical is organic and nonpolar. Rohm and Haas and Pennwalt have responded for their unregistered Ts, and data are adequate.

8. Du Pont has responded to data requirements for its unregistered T; however additional data are required pertaining to the stability of the technical at elevated temperatures, to metal ions and metals, and sensitivity to sunlight. Pennwalt has responded for its unregistered T, and data are adequate. The Agency has determined that this requirement does not apply to the Rohm and Haas unregistered T as it is never isolated from the manufacturing process of the FI.

TABLE B. PRODUCT SPECIFIC DATA REQUIREMENTS FOR MANCOZEB MANUFACTURING-USE PRODUCTS.[1]

Data Requirement	Test Substance[2]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[3]	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
40 CFR §158.155-190 Product Chemistry				
Product Composition				
61-1. Product Composition	MP	Yes	40373401 40381201 40391801 40517502	No
61-2. Beginning Materials & Production/Formulation Process	MP	Partially	40373401 40381201 40391801 40517502	Yes[4]
61-3. Formation of Impurities	MP	Partially	40373401 40381201 40391801 40517502	Yes[5]
Analysis and Certification of Product Ingredients				
62-1. Preliminary Analysis	MP	Partially	40620701 40652201 40678201 41220401	Yes[6]
62-2. Certified Limits	MP	Partially	40381201 40605901 40620701 40652201 40678201 41220401	Yes[7]
62-3. Enforcement Analytical Methods	MP	Partially	40517501 40605901 40620701 40652201 40678201 41220401 41357901	Yes[8]
Physical and Chemical Characteristics[9]				
63-2. Color	MP	Yes	40373402 40381202 40391801 40517502	No
63-3. Physical State	MP	Yes	40373402 40381202 40391801 40517502	No
63-4. Odor	MP	Yes	40373402 40381202 40391801 40517502	No
63-7. Density, Bulk Density, or Specific Gravity	MP	Partially	40373402 40381202 40391801 40517502	Yes[10]

(Continued, footnotes follow)

TABLE B. (Continued).

Data Requirement	Test Substance	Does EPA have data to satisfy this requirement?	Bibliographic Citation	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
63-12. pH	MP	Partially	40373402 40381202 40391801 40517502	Yes[11]
62-14. Oxidizing or Reducing Action	MP	Partially	40373402	Yes[12]
62-15. Flammability	MP	Partially	40373402	Yes[13]
63-16. Explodability	MP	Partially	40373402	Yes[14]
63-17. Storage Stability	MP	Partially	40373402	Yes[15]
63-18. Viscosity	MP	N/A	N/A	No
63-19. Miscibility	MP	N/A	N/A	No
63-20. Corrosion Characteristics	MP	Partially	40373402	Yes[15]
Other Requirements:				
64-1. Submittal of Samples	N/A	N/A	N/A	No

1. Data requirements pertain to the Rohm and Haas 80% FI (EPA Reg. No. 707-102) and the unregistered Ts produced by Du Pont and Pennwalt. The Agency has determined that because the Rohm and Haas unregistered T is never isolated from the manufacturing process of the FI, data requirements for an MP are not applicable. Additional data requirements are listed in the preceding Table A, "Generic Data Requirements for the Mancozeb Technical Grade of the Active Ingredient".

2. Test substance: PAI = purified active ingredient; TGAI = technical grade of the active ingredient; MP = manufacturing-use product.

3. Underlining indicates documents that have been reviewed in this Update Document.

4. Rohm and Haas has responded to data requirements for the 80% FI; however additional information must be provided regarding the relative amounts of starting materials, the equipment used to produce the product, reaction conditions, the duration of each step of the process, purification procedures, and quality control measures. Du Pont and Pennwalt have responded for their unregistered Ts, and data are adequate.

TABLE B. (Continued).

5. Rohm and Haas has responded to data requirements for the 80% FI; however additional information must be provided regarding a complete theoretical discussion of potential impurities based on post-production reactions between components of the product or its packaging. Du Pont and Pennwalt have responded for their unregistered Ts, and data are adequate.

6. Rohm and Haas has responded to data requirements for the 80% FI, and Du Pont and Pennwalt have responded for their unregistered Ts; however compositional analysis must be provided for five or more representative samples of the product, including their impurities, using methods which distinguish mancozeb per se from other potential carbon disulfide producing contaminants. Complete and detailed descriptions of the methods used for sample analysis must be submitted, including statements of their precision and accuracy.

7. Rohm and Haas has responded to data requirements for the 80% FI, and Du Pont and Pennwalt have responded for their unregistered Ts; however certified limits must be established using methods which distinguish mancozeb per se from other potential carbon disulfide producing contaminants. In addition the following are required: (i) the upper certified limit for an inert ingredient on the CSF of the 80% FI must be corrected or qualified as it disagrees with an earlier value; (ii) upper certified limits must be proposed for all impurities of toxicological concern in the Du Pont unregistered T; and (iii) certified limits must be established for the nitrosamines in the Pennwalt unregistered T using a validated method. Certifications must be submitted on EPA Form 8570-4 (Rev. 2/85).

8. Rohm and Haas has responded to data requirements for the 80% FI, and Du Pont and Pennwalt have responded for their unregistered Ts; however an enforcement analytical method capable of distinguishing mancozeb per se from other potential carbon disulfide producing contaminants must be provided. Analytical methods which are suitable for enforcement purposes must be provided for each active ingredient and each additional ingredient or impurity that is determined to be toxicologically significant. Suitability for enforcement purposes shall be determined from validation studies of method accuracy and precision submitted by the registrant.

9. As required in 40 CFR §158.190 and more fully described in the Pesticide Assessment Guidelines, Subdivision D, Guidelines Reference Nos. 63-2 through 63-20, data must be submitted on physicochemical characteristics of each manufacturing-use product (color, physical state, odor, specific gravity, pH, oxidizing or reducing action, flammability, explodability, storage stability, viscosity, miscibility, and corrosion characteristics). Additional data requirements regarding physicochemical properties of manufacturing-use products which contain only the technical grade of the active ingredient are listed in Table A, "Generic Data Requirements for the Mancozeb Technical Grade of the Active Ingredient."

TABLE B. (Continued).

10. Rohm and Haas has responded to data requirements for the 80% FI; however the temperature, units of measurement, and the method used must be specified. Du Pont and Pennwalt have responded for their unregistered Ts, and data are adequate.

11. Rohm and Haas has responded to data requirements for the 80% FI; however the temperature must be specified. Du Pont and Pennwalt have responded for their unregistered Ts, and data are adequate.

12. Du Pont and Pennwalt have not responded for their unregistered Ts; data are required on oxidizing/reducing potential if the product contains an oxidizing or reducing agent. Rohm and Haas has responded for the 80% FI, and data are adequate.

13. Du Pont and Pennwalt have not responded for their unregistered Ts; data are required on flammability if the product contains combustible liquids. Rohm and Haas has responded for the 80% FI, and data are adequate.

14. Du Pont and Pennwalt have not responded for their unregistered Ts; data are required if the product is potentially explosive. Rohm and Haas has responded for the 80% FI, and data are adequate.

15. Du Pont and Pennwalt have not responded for their unregistered Ts; data are required for this topic. Rohm and Haas has responded for the 80% FI, and data are adequate.

DYNAMAC
CORPORATION
Environmental Services

Final Report

MANCOZEB (CBRS No. 7466, 7959 and 8514) Shaughnessy No. 014504 Task 3: Reregistration Standard Update

April 27, 1992

Contract No. 68-D2-0053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
2275 Research Boulevard
Rockville, MD 20850-3268

MANCOZEB

SHAUGHNESSY NUMBER 014504

REREGISTRATION STANDARD UPDATE (CBRS NO. 7466)

RESIDUE CHEMISTRY

Task - 3

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MANCOZEB

SHAUGHNESSY NUMBER 014504

REREGISTRATION STANDARD UPDATE (CBRS NO. 7466)

RESIDUE CHEMISTRY

Task - 3

BACKGROUND

In 1977, the Agency initiated a Rebuttable Presumption: Against Registration (RPAR; now called Special Review) and Continued Registration of Pesticide Products containing ethylene bisdithiocarbamates (EBDCs); mancozeb belongs to the EBDC group of fungicides. The need for Special Review of the EBDCs was based on evidence suggesting that the EBDCs and ethylenethiourea (ETU), a metabolite and degradation product of these pesticides posed potential risks to human health and the environment. In 1982, the Agency concluded this Special Review by issuing a Final Determination (PD 4) which required risk reduction measures to prevent unreasonable adverse effects pending development and submission of additional data needed for improved risk assessment.

In 1987, EPA issued a second Notice of Initiation of Special Review of the EBDC pesticides because of health concerns caused by ETU. The Preliminary Determination (PD 2/3 was published 12/20/89 (54 FR 52158). The Final Determination for this Special Review (PD 4) was published in the Federal Register (57 FR 7484, 3/2/92). It was determined that the dietary risks of EBDCs exceed the benefits for the following food/feed uses for which one or more of the EBDC pesticides are registered: apricots, carrots, celery, collards, mustard greens, nectarines, peaches, rhubarb, spinach, succulent beans, and turnips; accordingly, EPA intends to cancel all mancozeb and other EBDC products registered on these food/feed crops. In addition, the Agency intends to cancel products registered for other food/feed crops unless registrants amend their product labels to reflect changes in use pattern specified in the EBDC PD 4. The use patterns allowed by the EBDC PD 4 are presented in this Update document under "MAGNITUDE OF THE RESIDUE IN PLANTS" section. Tolerance reductions and revocations were proposed to coordinate with the proposed cancellations in the Preliminary Determination (55 FR 20416, 5/16/90 and 55 FR 34289, 8/22/90).

INTRODUCTION

The EPA Site Listing (SP05) dated 9/17/90 and the EPA Compendium of Acceptable Uses dated 10/30/84 identified registered food/feed uses for the fungicide mancozeb (zinc ethylenebisdithiocarbamate) on the following crops: apples, asparagus, bananas, barley, carrots, celery, corn (field, sweet, and popcorn), cotton, crabapples, cranberries, cucumbers, fennel, grapes, melons, oats, onions, papayas, peanuts, pears, potatoes, quinces, rye, summer squash, sugar beets, tomatoes, walnuts, and wheat. Mancozeb is also registered for seed, seed piece, planting stock, or propagation stock treatments on flaxseed, pineapples, rice, safflower, and sorghum. The EPA site listing for Special Local Needs registration (SLN-1), dated 9/17/90, additionally identified almonds and pumpkins as registered sites. The non-food uses of mancozeb include caprifigs, tobacco, and ornamental plants. Mancozeb formulations registered for use on the crops listed above include the 40, 48, 62, 70, and 80% wettable powder (WP), 30, 32, 37, and 80% flowable concentrate (FlC), 70 and 75% dry flowable (DF), and the 3.2, 4, 4.8, 6, 6.4, 8, and 50% dust (D). Applications are typically made as foliar, soil, seed, and dip treatments.

The Mancozeb Reregistration Guidance Document, dated 4/87, identified outstanding residue chemistry data requirements for metabolism in plants and animals, residue analytical methods, and storage stability; and required additional crop field trials depicting residues of mancozeb, ETU and other residues of concern in or on apples, asparagus, bananas, carrots, celery, corn, cottonseed, cranberries, cucumbers, fennel, grapes, melons, onions, papayas, peanuts, pears, potatoes, sugar beet (roots and tops), summer squash, tobacco, tomatoes, and wheat. Additional data were required for processed products of corn, cottonseed, grapes, peanuts, potatoes, and sugar beets. The Guidance Document also required residue data and proposal of tolerances to support registered seed or planting/propagation stock uses on caprifigs, flax, pineapples, rice, safflower, and sorghum.

Since issuance of the Guidance Document, the Mancozeb Task Force [Rohm and Haas, Ciba-Geigy, E.I. du Pont, and Atochem (formerly Pennwalt)] have submitted several studies to support the reregistration of mancozeb; these submissions are detailed by topic below:

Topic	MRID(s)
Plant metabolism	41095201
Residue analytical methods	40764601, 41343101[a]
Storage stability	41070001[b], 41976101[c]
Crop field trials and/or processing studies	
Apples	41092007
Asparagus	40869701, 40869702
Bananas	40913303, 40913304
Beans	40118201[d]
Carrots	40869703
Corn (sweet, grain, pop)	40869705, 41093201, 41091701, 42155901[e]
Cucumbers	40869707, 41092006
Cranberries	40869706
Grapes	41092001, 41092002, 41150101[f], 41483801
Lettuce	40118201[d]
Onions	40869708, 41092003
Papayas	40869709, 40869710
Peanuts	40869711, 41092004, 41844802
Pears	40913305, 40913306
Peppers	40118201[d]
Potatoes	40913301, 41091601
Sugar beets	40869712
Tomatoes	40768001, 40869713, 40869714, 41443201, 41844801
Wheat	40869715, 40869716, 41092005
Seed treatments	41091801, 40869717

[a] Reviewed under CBRS Nos. 6357, 6358, and 6359 (S. Hummel, 7/16/90).
[b] Reviewed under CBRS No. 5280 (S. Hummel, 8/17/89).
[c] Reviewed in this document under CBRS No. 8514.
[d] Reviewed under CBRS No. 2654 (M. Kovacs, 12/10/87).
[e] Reviewed in this document under CBRS No. 9250.
[f] Reviewed under CBTS Nos. 5557 and 5558 (G. Otakie, 12/11/89).

Additional residue chemistry data were also submitted by the ETU Task Force in response to a Special Review Data-Call-In Notice issued 3/31/88 (market basket survey; EBDC/ETU monitoring study). The first and second interim reports (MRIDs 41383301, 41452201,

41480601, and 41511801) which included method validation and residue data were reviewed by S. Hummel (EPA Memoranda CBRS Nos. 6546 through -8, 6671 through -3, 6726 through -8, and 6757 through -9, all dated 8/13/90). The fourth quarter/final report (MRID 41643601) was also reviewed by S. Hummel (DEB No. 7155, dated 12/4/90).

Tolerances are expressed in terms of residues of mancozeb per se (a coordination product of zinc ion and maneb, manganous ethylenebisdithiocarbamate) in or on raw agricultural commodities and processed foods [40 CFR §180.176, §180.319, §185.6300, and §186.6300].

SUMMARY

The following Mancozeb Residue Chemistry data are required:

- Additional data pertaining to plant and animal metabolism.
- Storage stability data to support any residue data required in this document.
- Label revisions to reflect the use patterns allowed by EBDC PD 4 on food/feed crops eligible for reregistration.
- Additional field residue data are required for apples, asparagus, bananas, barley grain, barley straw, corn (sweet, pop, and field), corn forage and fodder, cottonseed, crabapples, cranberries, cucumbers, fennel, grapes, kidney, liver, melons, oat grain, oat straw, onions (dry bulb), peanuts, pears, potatoes, quinces, rye grain, rye straw, squash (summer), sugar beets, sugar beet tops, tomatoes, and wheat grain.
- Additional processing data are required for field corn, sweet corn, cottonseed, potatoes, rice, sugar beets, and the crops grown from treated seed (flax, pineapples, rice, safflower, and sorghum).
- Higher tolerances must be proposed for papayas and wheat straw. Alternatively, the use pattern may be modified such that tolerance exceeding residues will not occur.
- The established tolerances for residues of mancozeb in or on carrots and celery should be revoked since mancozeb is not allowed by PD 4 to be used on these crops.

The need for tolerances to cover seed treatments will be reevaluated when the nature of the residue is adequately understood.

QUALITATIVE NATURE OF THE RESIDUE IN PLANTS

Conclusions:

The Mancozeb Guidance Document, dated 4/87, concluded that additional data are required depicting the uptake, distribution, and metabolism of mancozeb in pome fruits and fruiting vegetable crops with sampling intervals through at least 21 days. In addition, the Guidance Document required representative samples from these tests to be analyzed by enforcement methods to ascertain that these methods are capable of determining all metabolites of concern.

In response to the Guidance Document requirements, Rohm and Haas submitted a metabolism study in which tomatoes (MRID 41095201) received multiple foliar applications of ethylene-labeled [^{14}C]mancozeb. These data do not adequately explain the qualitative nature of the residue in tomatoes because ethyleneurea (EU), accounting for ca. 10% of the TRR, was the only metabolite for which the identity was adequately confirmed. The registrant must confirm the identifications of metabolites by a second method such as GC or MS. The identity of ca. 60% of the residue in tomato fruits characterized as natural products such as lipids, carbohydrates, and amino acids in tomato fruit is considered putative; the incorporation of [^{14}C]mancozeb into natural products must be verified by confirmatory analysis.

Residues of mancozeb and ETU were nondetectable (<0.05 and 0.01 ppm, respectively) in or on tomato samples from the tomato metabolism study analyzed using the enforcement methods. The registrant needs to submit information regarding the intervals and conditions of sample storage.

Rohm and Haas Company additionally submitted letters, dated 6/26/87 and 7/9/87, clarifying previously submitted soybean, sugar beet and wheat metabolism studies and addressing the deficiencies identified in the Residue Chemistry Chapter and Update. The registrant contends that the metabolic decomposition of mancozeb in soybeans, sugar beets, and wheat is similar. The major metabolites were natural products (proteins, carbohydrates, lipids, and lignins) with small amounts of mancozeb degradation products (ETU, EU, EBIS, JB, and EDA). The registrant submitted a summary in tabular form of the metabolites identified in soybeans (beans and pods), sugar beets (tops and roots), and wheat (seed, chaff, and straw). Diagrams of the fractionation schemes of sugar beets (leaf/stem) and wheat (seed, chaff, and straw) were also submitted. The registrant contends that ca. 80% of the activity in sugar beet tops was characterized by chemical and chromatographic behavior. The registrant stated that 57% of the radiolabel in wheat seed, 80% in wheat straw, and 35% in wheat chaff tissue was characterized and that the unextractable

label was considered to be polymeric natural products and the identity of the fraction was not pursued. No new metabolism data were submitted for these crops. After reexamining the soybean, sugar beet, and wheat metabolism studies, we conclude that the nature of the residue in these crops remains inadequately understood because of lack of confirmatory analyses.

Regarding the soybean study (MRIDs 00152696 and 00164509), ca. 45% of the TRR in soybean pods was identified as degradates or natural products and ca. 30% of the TRR in soybeans was identified as natural products; these identifications must be considered tentative, since no confirmatory analyses were conducted. Although two TLC systems and two HPLC columns were used, peaks/spots from standards of mancozeb degradates overlapped peaks/spots from standards of sugars and amino acids. No data were submitted regarding the nature of the residue in soybean forage or hay. In addition, we note that mancozeb currently is not registered for use on soybeans.

Regarding the sugar beet metabolism study (MRID 00156715), the identification of ^{14}C-activity in sugar beet roots and tops as known degradates and natural products must be considered tentative because no confirmatory analyses were conducted. The use of fraction collecting with HPLC degraded the resolution to the point where no identifications could be made. Approximately 70% of the TRR in sugar beet tops and 50% of the TRR in roots were not analyzed.

In the wheat metabolism study (MRIDs 00160703 and 00164510), ca. 20% of the TRR in seed and chaff were tentatively identified as known degradates and ca. 10-30% as natural products. No confirmatory analyses were conducted and TLC analysis of the ethanol extracts (accounting for ca. 20% of the TRR for seed and chaff) by both reverse phase and normal phase were inconclusive because of poor separation.

An Agency evaluation (EPA Memorandum CBRS No. 4015, S. Hummel, dated 9/27/88) of data deficiencies for plant metabolism concluded that the three crops chosen by Rohm and Haas (wheat, sugar beets, and soybeans) each account for <2% of the mancozeb use and that samples for the previously submitted metabolism studies (wheat and soybeans) were taken over 45 days after the last treatment. In this same memorandum, it was noted that metabolism studies on a fruiting vegetable crop and possibly a pome fruit crop are needed because of the large amount of mancozeb used on these types of crops. Table 1 depicts the molecular structures of mancozeb and some of its possible metabolites/degradates. The following additional data are required:

- For the submitted tomato metabolism study (MRID 41095201), the registrant must confirm the identifications of metabolites by a second method such as GC or MS. The identity of ca. 60% of the residue characterized as natural products such as lipids, carbohydrates, and amino acids in tomato fruit is considered putative; the incorporation of [^{14}C]mancozeb into natural products must be verified. The registrant must submit information regarding the intervals and conditions of sample storage.

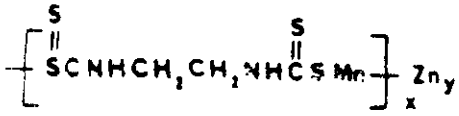
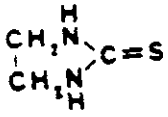
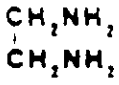
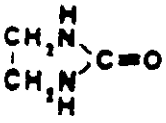
- Data depicting the uptake, distribution, and metabolism of [^{14}C]mancozeb in a pome fruit (apples) and in a grain crop. A completely characterized test substance must be applied under conditions representing normal cropping practices and at rates high enough to permit characterization of ^{14}C-residues. The identities and quantities of residues in mature plant parts must be determined in order to elucidate terminal residues. Data depicting all terminal residue components in commodities at the time of harvest should be expressed as the percentage of the total recovered radioactivity and concentration (ppm). Confirmation of the identities of residue using a suitable method such as MS or HPLC is also required. Representative samples from these studies must also be analyzed by the residues analytical methods developed for data collection and tolerance enforcement to ascertain that these methods are capable of adequately recovering all metabolites of concern.

- Confirmatory analyses for metabolites reported in the other metabolism studies. Confirmatory analyses are required for the wheat or soybean metabolism study. Confirmatory analyses are required for the sugar beet metabolism study.

References (used):

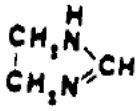
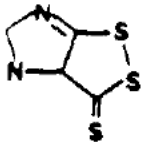
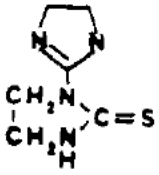
MRID(s): 00152696. 00156715. 00160703. 00164509. 00164510. 41095201.

Table 1. Mancozeb and its metabolites in plants and animals.

Code	Chemical name Structure	Substrate	MRID Common name
I	Zinc ion and manganese ethylene bisdithiocarbamate 		Mancozeb
II	Ethylenethiourea 	Soybeans	00152696
		Goat liver, muscle, and milk	00160780
		Goat kidney	00164880
		Poultry eggs, liver, and kidney	00164879
			ETU
III	Ethylenediamine 	Wheat straw	00164510
		Sugar beet tops	00156715
		Soybeans	00152696
		Goat liver, muscle, and milk[a]	00160780
		Poultry eggs, kidney, muscle, and liver[a]	00164879
			EDA
IV	Ethyleneurea 	Wheat straw	00164510
		Sugar beet tops	00156715
		Soybeans	00152696
		Goat liver, muscle, and milk[a]	00160780
		Poultry eggs, liver, kidney, and muscle[a]	00164879
		Tomato fruit	41095201
			EU

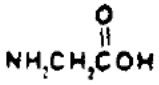
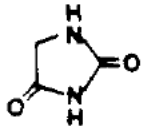
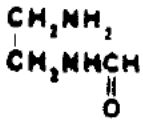
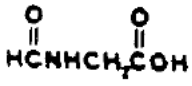
(Continued).

Table 1. (Continued).

Code	Chemical name Structure	Substrate	MRID Common name
V	2-imidazoline 	Sugar beet tops	00156715
		Wheat straw	00164510
		Poultry eggs, liver, and muscle[a]	00164879
			IMD
VI	Ethylene bisisocyanate sulfide 	Sugar beet tops	00156715
		Wheat straw	00164510
		Soybeans	00152696
		Poultry eggs, liver, and kidney[a]	00164879
		Goat liver and muscle[a]	00160780
			EBIS
VII	3-(2-imidazolin-2-yl)-2-imidazolidinethione 	Sugar beet tops	00156715
		Soybeans	00152696
		Poultry eggs, liver, and kidney[a]	00164879
			Jaffe's Base (JB)

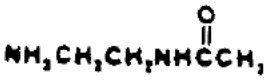
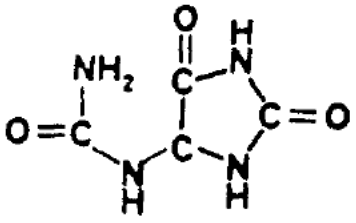
(Continued).

Table 1. (Continued).

Code	Chemical name Structure	Substrate	MRID Common name
VIII	Glycine 	Goat liver and muscle[a]	00160780
		Poultry eggs, liver, muscle, and kidney[a]	00164879
IX	Hydantoin 	Soybeans	00152696
		Sugar beet tops	00156715
		Poultry eggs, liver, kidney, and muscle[a]	00164879
		Goat muscle and liver[a]	00160780 HT
X	N-formyl-ethylene-diamine 	Sugar beet tops	00156715 N-formyl-EDA
XI	N-formylglycine 	Goat liver, muscle, and milk[d]	00160780

(Continued).

Table 1. (Continued).

Code	Chemical name Structure	Substrate	MRID Common name
XII	N-acetylethylene-diamine 	Goat liver, muscle, and milk[a]	00160780
		Poultry eggs, kidney, muscle, and liver[a]	00164879
XIII	Allantoin 	Goat liver, kidney, and muscle[a]	0160780

[a]Tentative metabolite identifications because of poor TLC resolution and/or no confirmatory procedures were performed.

Discussion of the data:

Tomatoes: Rohm and Haas (1989; MRID 41095201) submitted data pertaining to the metabolism of [^{14}C]mancozeb in tomatoes. Tomato plants received nine foliar applications at approximately 7-day intervals with ethylene-labeled [^{14}C]mancozeb (9.61 mCi/g specific activity and 88% radiopurity) at 2.4 lb ai/A/application. Tomatoes were sampled just prior to the fourth, sixth, seventh, eighth, and ninth applications, and 5 days following the final treatment. [Note: Rohm and Haas' proposed protocol (5/4/88) to utilize a 5-day sample interval rather than the 21-day interval required in the Guidance Document was reviewed and accepted, provided multiple applications were made (EPA Memorandum CBRS No. 4656, 4707, and 4995, S. Hummel, dated 10/25/90).]

Total Radioactive Residues

Tomato fruit samples were analyzed for total radioactive residues (TRR) by liquid scintillation spectrometry (LSS) following homogenization in dry ice and combustion (Packard Tri-Carb Sample Oxidizer). Total radioactive residues (TRR) were 0.54-0.79 ppm in four of the samples collected during the trial; one additional sample collected between the seventh and eighth applications bore TRR of 0.07 ppm. The TRR in the final harvest sample was 0.66 ppm; this sample was used for residue characterization.

Extraction

Homogenized tomato was filtered and the filtrate mixed with ethanol (a sediment resulting after the addition of ethanol contained no radioactivity and was discarded). The initial aqueous phase (47.4% of the TRR), was cleaned-up using a Superclean LC-18 column preconditioned with methanol, and residues were eluted with water followed by methanol:water (1:1, v:v). Nonradioactive impurities were precipitated by addition of ethanol and removed by centrifugation. ^{14}C-Residues in the purified methanol:water fractions were radioassayed (LSS).

The solids from the initial aqueous extraction were extracted sequentially using chloroform, methanol, 1 N potassium hydroxide, and 1 N hydrochloric acid. The unextracted solid residues were subjected to treatment using hot (80 C) 1 N potassium hydroxide for 2 hours. Extracts were radioassayed (LSS). Chloroform solubilized 5.2% of the TRR (nonpolar lipids), 9% was methanol-soluble (polar lipids), 18.7% was potassium hydroxide-soluble, and 3% of the TRR was hydrochloric acid-soluble. Following extraction with hydrochloric acid, 16.6% of the TRR remained insoluble. An additional 7.8% of the TRR was rendered soluble by the hot alkaline treatment; 8.8% of the TRR remained unextractable and was not characterized further.

Characterization/Identification

Aliquots of the purified aqueous fraction were analyzed using normal phase TLC on silica gel plates developed with solvent systems of ethyl acetate:2-propanol:water (65:25:10, v:v:v) and ethyl acetate:ethanol:ammonium hydroxide (3:1:1, v:v:v). Ten non-radiolabeled reference standards [ETU, EU, EBIS, EDA, IMD, N-acetylethylenediamine, hydantoin, glycine, glutamic acid, and aspartic acid] were co-chromatographed with the aqueous fractions. Reference standards were visualized colorimetrically using the following spray reagents:

(i) 0.5% *p*-dimethyl-aminocinnamaldehyde in ethanol:4N hydrochloric acid (3:1, v:v) (for EBIS, ETU, and EU);

(ii) FN Reagent; 10% sodium hydroxide:10% sodium nitroferricyanide:10%potassium ferricyanide:water (1:1:1:3, v:v:v:v) (for EBIS, EDA, ETU, EU, hydantoin, and IMD);

(iii) 0.1% Ninhydrin Spray Reagent (for aspartic acid, glutamic acid, and glycine); and

(iv) 0.5% Fluorescamine in acetone (for aspartic acid, N-acetylethylenediamine, EDA, glutamic acid, and glycine).

Radiolabeled aqueous-soluble residues were visualized using Kodak SB-5 X-ray film that was exposed in dark, sealed carriers to TLC plates bearing radioactive residues for 7 to 21 days. The film was developed according to standard wet chemical film development techniques. Residues were quantified by scraping radioactive regions on the TLC plate into vials containing Hydrofluor and analyzing by LSS. Residues in the purified aqueous fraction did not move from the baseline using either solvent system. Residues were also characterized by size-exclusion chromatography (SEC). The SEC analysis indicated that this fraction was composed of high molecular weight compounds. Aliquots were also hydrolyzed with protease and pectinase as follows.

An aliquot of the purified aqueous fraction was digested with protease at pH 8, overnight at ambient temperature. SEC of the hydrolyzed fraction indicated a decrease in the molecular size of the radioactive components. The protease-treated aqueous fraction was derivatized with dansyl chloride. Derivatized residues were analyzed using TLC (same conditions as stated above). Approximately 64% of the radioactivity remained at the origin or in the pre-adsorbent zone. The remaining radioactivity, was distributed in bands and was assumed to be dansylated amino acids. The derivatized residues were analyzed using high performance liquid chromatography (HPLC) with an amino acid analysis system (gradient elution) using 25 mM potassium hydroxide at pH 6.8 and acetonitrile:2-propanol (75:25, v:v) on a

reverse phase column equipped with a flow-through radioactivity detector. HPLC analysis resulted in fractions cochromatographing with dansyl-aspartic:glutamic acids and dansyl-glycine. Raw data for the HPLC analysis were not included in the submission.

A second aliquot of the aqueous fraction was incubated overnight with pectinase at pH 4 at ambient temperature. SEC of the fraction following hydrolysis indicated a decrease in the molecular size of the radioactive components. The pectinase hydrolysate was partitioned with ethyl acetate and the aqueous layer was mixed with reagent alcohol and concentrated to near dryness. The ^{14}C-residues were derivatized with acetic anhydride. The mixture was heated for 2 hours at 100 C and partitioned with methylene chloride. The methylene chloride fraction was analyzed using TLC (same conditions as stated above). On the TLC plate, this material moved as a broad band which the registrant states is consistent with methyl tetra-O-acetylgalacturonate. No confirmatory analyses were performed.

The methanol-, chloroform-, and hydrochloric acid-soluble fractions were analyzed by normal phase TLC (same conditions as stated above). Residues were not separated by TLC and none were identified, the autoradiography indicated that the residues migrated with the mass. The potassium hydroxide (room temperature) fraction was neutralized (pH 7 with HCl) and residues were separated using TLC on silica gel plates developed with ethanol:concentrated ammonium hydroxide; the radioactive zones determined by Ambis scanner. Two zones were identified. The major zone (12.9% of the TRR) co-chromatographed with ethyleneurea (EU) and the second zone was not identified. The identity of EU in the first zone was confirmed by GC/MS using a HP-1 column (methyl silicone on fused silica) and an unspecified ionization source.

The distribution and tentative characterization of mancozeb metabolites in tomato fruit is presented in Table 2. Ethyleneurea, accounting for ca. 13% of the TRR, was the only metabolite identified and confirmed by two analytical methods.

Table 2. Tentative characterization of ^{14}C-activity in tomato fruit following multiple foliar applications with [^{14}C]mancozeb.

Fraction/component	% of TRR	ppm [^{14}C]-equivalents
Aqueous fraction:	(47.4)[a]	
protease digested	14.2	0.09
pectinase digested	(33.2)	0.22
sugars	20.9	
other carbohydrates	12.3	
Chloroform-soluble	5.2	0.03
Methanol-soluble	9.0	0.06
Potassium hydroxide-soluble	(18.7)	
ethyleneurea	12.9	0.09
unknown	5.8	0.04
Hydrochloric acid-soluble	3.0	0.02
Hot potassium hydroxide-soluble	7.8	0.05
Nonextractable	8.8	0.06
Total	99.9	0.66

Summary of tentative residue characterization in tomato:

Ethyleneurea	12.9%
Putative natural components	(61.6%)
unidentified organosoluble	14.2%
unidentified carbohydrates	12.2%
unidentified sugars	20.0%
Unknown protease digested	14.2%
Unidentified KOH-soluble	5.8%
Not analyzed	19.6%

[a] The % of the TRR in the fractions prior to further analysis are given in parentheses.

Enforcement analytical methods - Mancozeb and ETU

Tomato samples from the final harvest were analyzed for the presence of mancozeb and ETU using the currently available enforcement methods. Data depicting residues of mancozeb were analyzed using a colorimetric method (Pease as modified by Keppel) with a limit of detection of 0.05 ppm and for ETU using a GLC method (Onley) with a limit of detection of 0.01 ppm. Residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on one tomato sample. Recovery was 90.4-97.5% from three samples fortified with mancozeb at 0.03-0.06 ppm and was 80-88.5% from three samples fortified with ETU at 0.01-0.02 ppm. We note that the registrant has also submitted

field trial data (see "MAGNITUDE OF THE RESIDUE IN PLANTS" section) which indicate that mancozeb and ETU are present at detectable levels in or on tomatoes stored frozen prior to analysis for up to ca. 330 days. The registrant must submit the condition and interval of storage for tomato samples from this study.

The nature of the residue in tomatoes is not adequately understood because the only metabolite for which the identity was adequately confirmed was ethyleneurea (ca. 13% of the TRR) and ca. 25% of the residue was not characterized at all. The characterization of 62% of the residue characterized as natural products (lipids, carbohydrates, and amino acids) is considered putative because the identities of these residues were not subjected to confirmatory analyses. We also note that mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm) in or on tomatoes analyzed using the enforcement methods. Considering the instability of mancozeb and ETU in plant samples during frozen storage, the registrant must submit the interval of storage and conditions of storage for tomato samples in this study.

Reevaluation of Previously Submitted Plant Metabolism Studies

The metabolism studies on soybeans, sugar beets, and wheat have been previously submitted and were discussed in the Residue Chemistry Chapter of the Mancozeb Registration Standard. These data are resummarized here in tabular format for clarity and continuity.

Soybeans: Mancozeb Task Force submitted data (MRID 00152696, Rohm and Haas Report No. 31L-85-18 and MRID 00164509, Rohm and Haas Report No. 310-86-55). Soybeans were harvested 56 days following the last of two foliar applications with [^{14}C]mancozeb at ca. 3 lb ai/A. The proposed use for soybeans is multiple foliar applications with a 35-day PHI. Soybean plants were harvested, and total radioactive residues (TRR) determined by liquid scintillation spectrometry (LSS) following combustion. Of the radioactivity recovered, 32% was in the bean, 36% in the pods, and 32% in the stem/stalk. Beans and pods were subjected to further characterization. Residues in the stem/stalk were assumed to be similar to those in the pods, and were not subjected to additional analysis. Samples of beans and pods were analyzed for mancozeb (CS_2 evolution method, GLC, Report No. TR36F-82-20) and for ETU (GLC, Haines and Adler, 1972) (Table 3).

Table 3. Total radioactive residues (ppm mancozeb equivalents) in soybeans harvested following foliar applications with [^{14}C]mancozeb.

	Residue (ppm mancozeb)		
Item	TRR	CS_2	ETU
Beans	2.3	<0.07	<0.014
Pods	14.01	1.34	<0.014

Soybean pods. Approximately 36% of the TRR in soybean pods was extractable with methanol:chloroform:water. Following extraction with additional chloroform, 4% of the TRR was partitioned into the chloroform fraction and 32% of the TRR remained in the methanol:water fraction. The chloroform fraction was not analyzed. The methanol:chloroform:water fraction (64% of the TRR) was not further analyzed in the initial report (Rohm and Haas Report No. 31L-85-18).

The methanol:water fraction was cleaned-up using a Sep-Pak C-18 column. Aliquots of this fraction were analyzed by reverse phase TLC on C-18 plates developed with methanol:water and by normal phase TLC on silica gel plates developed with ethyl acetate:i-propanol:water. The radioactive zones were scraped and counted. The residues identified in the methanol:water fraction were: hydantoin (0-11%), Jaffe's base (JB) (31-42%), ethylene bisisothiocyanate sulfide (EBIS) (12-13%), and ethyleneurea (EU) (15-16%). In addition, 13-20% were considered unknown and 0-9% other using the two TLC analyses. There was no evidence of confirmation of these identifications by a confirmatory method of analysis.

The methanol:chloroform:water insoluble residues (64% of the TRR) in soybean pods were extracted with dilute acid and hot water (MRID No. 00164509, Rohm and Haas Report No. 310-86-55). Dilute acid (2M HCl) extracted 16% of the TRR and hot water extracted 23% of the TRR. Both extracts were cleaned-up using anion and cation exchange columns. From the dilute acid extract, 3.4% of the TRR eluted through both the cation and anion exchange columns, 2% was washed off the cation column using 6M HCl, 3% was washed off the anion column using 6M HCl, and 8% remained on the ion exchange columns. From the hot water extract, 10.5% of the TRR eluted through both the cation and anion exchange columns, 2% was washed off the cation column using 6M HCl, 2% was washed off the anion column using 6M HCl, and 8% remained on the ion exchange columns. Only the initial eluates were further characterized. These initial radioactive eluates were analyzed using two HPLC systems with two different columns and detection methods. The first system separated putative sugars using a HPX-

87C cation exchange column and a Refractive Index (RI) detector; the mobile phase was 100% water for both pod and bean analyses. The second system separated the radiolabeled residues using a ERMA amine-modified silica column and equipped with a fraction collector; fractions were subsequently analyzed for radioactivity by LSS. In system two, the mobile phase was acetonitrile:water (75:25, v:v) for pod residues, and acetonitrile:water (60:40, v:v) for soybean sugars. In both systems, the registrant stated that sugars were tentatively identified by comparing retention times of the residues against sugar reference standards (listed below). The methods by which the extracted residues were identified in the collected fractions from system two were not presented. Approximately 33% of the hot water extract had retention times on both HPLC columns similar to reference standards (sucrose, fructose, glucose, raffinose, and stachyose), and 60% had longer retention times than the sugar reference standards on the HPX-87C column. Standards of ETU and EU eluted with retention times similar to the sugars. The radioactive residues were not further identified. No confirmatory analyses were conducted. The TLC spots of known mancozeb degradate standards and sugar standards overlapped and could not be used for purposes of metabolite identification. Although the non-radioactive sugar standards were well resolved by HPLC (0.5 minute peak widths), the radioactivity analyses were done by fraction collection (2 minute fractions), instead of directly coupling the radioactivity detector to the HPLC, so that the good resolution was lost.

The methanol:chloroform:water insoluble residues in soybean pods were also analyzed for lignin. Residues were extracted with 72% H_2SO_4, then refluxed with 3% H_2SO_4. The remaining residue (19% of the TRR) was subjected to elemental and IR analysis. The elemental analysis indicated a residue composition comparable to that of lignin. The IR spectrum showed the expected bands for lignin. These analyses indicate that the major part of the residue is lignin, but they do not prove that the radioactive residue in this fraction is actually lignin.

<u>Soybeans.</u> Approximately 53% of the TRR in soybeans was extractable with a mixture of methanol:chloroform:water. Following extraction with additional chloroform, 6% of the TRR was partitioned into the chloroform fraction and 47% of the TRR remained in the methanol:water insoluble fraction. The chloroform fraction and the methanol:chloroform:water fraction (47% of the TRR) were not subjected to further analysis. The methanol:water extract was analyzed by reverse phase TLC. None of the known mancozeb degradates were identified in the extract in the TLC analysis. The extract was not further analyzed. No base or enzyme hydrolysis was attempted.

The soybeans were also fractionated using a scheme designed to separate soybeans into its natural components. Samples were

extracted with hexane, followed by water. The hexane extract, which would contain oils, contained 10% of the TRR. This fraction appeared as a smear on a TLC plate, indicating that it contained many components. Residues on the TLC plate were visualized by radioautography. The water extract contained 59% of the TRR. Radioactivity in the extracts was determined by LSS. The insoluble residues (30% of the TRR) were not further analyzed.

Acetonitrile was added to the water extract to precipitate proteins (acid precipitated protein fraction). Excess acetonitrile was added and an oily residue removed. Acetonitrile was then removed under reduced pressure. The acid precipitated protein fraction (21% of the TRR) was not further analyzed. The water extract was cleaned up by HPLC (C-18 column) and anion exchange (SAX column). A total of 80% of the activity in the fraction eluted from the columns.

Ethanol was added to the eluate to precipitate carbohydrates (1% of the TRR). The eluate was then analyzed by Gel Permeation Chromatography (GPC, Gel Exclusion Chromatography, Size Exclusion Chromatography). For these analyses, ultraviolet (UV) and radioactivity detectors were connected in series. Reference standards were EDA, JB, ETU, and several high molecular weight proteins. EDA, JB, and ETU were not detected. Although not reported by the registrant, the extract appears to contain a single component. Additional analyses were conducted before and after dialysis designed to remove high molecular weight compounds. Approximately 9% of the TRR was classified as compounds with high molecular weights (>25,000) and were assumed to be proteins by the registrant.

The distribution and characterization of residues in soybean pods and soybeans are summarized in tabular form in Tables 4 and 5. Identifications must be considered tentative, since no confirmatory analyses were conducted. Although two TLC systems and two HPLC columns were used, peaks/spots from standards of mancozeb degradates overlapped peaks/spots from standards of sugars and amino acids. Soybean stem/stalk was not analyzed and was assumed to be similar to soybean pods.

Table 4. Tentative identification[a] of mancozeb metabolites in soybean pods (TRR = 14 ppm).

Item	Extract (%)	TRR %	TRR ppm[b]
Methanol:water extract		(32)	
Hydantoin	0-11	2	0.3
JB	31-42	12	1.7
EBIS	12-13	4	0.6
EU	15-16	5	0.7
Unknown	13-20	5	0.7
Other	0-9	3	0.4
Chloroform extract[c]		4	
Not extracted with methanol: chloroform:water		(64)[d]	
Water extract		(23)	
Elutes through anion & cation column (neutral)		10.5	
- Sugars	33	4	0.6
- Not identified	66	7	1.0
Acid wash or left on column[c]		12	1.7
Dissolved in sulfuric acid not included in water extract[c]		(45) 22	3.1
Solid remaining after treatment with conc. sulfuric acid (lignin)		19	2.7
Summary of Tentative Identifications in Soybean Pods[a]			
Known degradates[e]		(23)	
Natural products[f]		(23)	
Not identified/unknown		(15)	
Not analyzed		(38)	

[a] Identifications are considered tentative because no confirmatory analyses were done, except for hydantoin, JB, EBIS, and EU, which were analyzed by two different TLC systems.
[b] Residue in ppm mancozeb equivalents.
[c] Extract not analyzed.
[d] Results of further extractions follow in the table.
[e] Identified by TLC R_f.
[f] Identified by HPLC fraction or insoluble in concentrated sulfuric acid.

Table 5. Tentative identification of mancozeb metabolites in soybeans (TRR = 2.3 ppm)[a].

Item	Total radioactive residues %	ppm[b]
Hexane extract[c]	11	0.3
Water extract	(59)	
Sugars	18	0.4
Molecular weight >25000	9	0.2
Precipitated by acetonitrile[d]	21	0.4
Insoluble[d]	30	0.7
Summary of Tentative Identifications in Soybeans[a]		
Many components[c]	(11)	
Natural components	(27)	
Not identified	(11)	
Not analyzed	(51)	

[a] Identifications are considered tentative because no confirmatory analyses were done.
[b] Residue in ppm mancozeb equivalents.
[c] Many components, smear on TLC.
[d] Not analyzed.

Sugar Beets. The metabolism of mancozeb was discussed in Rohm and Haas Report No. 31L-86-08 (MRID 00156715). Sugar beets were harvested 14 days following the last of three applications of [^{14}C]mancozeb at 2 lb ai/A (18-31 day intervals). The registered use is multiple applications at 2.44 lb ai/A with a 14-day PHI. Samples were separated into leaf/stem and root, combusted, and subjected to LSS. Of the radioactivity recovered, 77% was in the leaf/stem and 23% was in the root. Samples were analyzed for mancozeb (CS_2 evolution method, GLC, Report No. TR36F-82-20) and for ETU (GLC, Haines and Adler, 1972); the results are presented below in Table 6.

Table 6. Total radioactive residues (ppm mancozeb equivalents) in sugar beets harvested following three applications of [^{14}C]mancozeb.

Item	Residue (ppm mancozeb equivalents) TRR	CS_2	ETU
Roots	0.5	<0.037	<0.014
Leaf/stem	9.5	0.69	<0.014

Sugar beet leaf/stem. The sugar beet leaf/stem fraction was extracted by procedures described for soybean pods. Approximately 73% of the TRR in the leaf/stem fraction was methanol:chloroform:water extractable. Following extraction with additional chloroform, 10% of the TRR was partitioned into the chloroform fraction and 63% of the TRR remained in the methanol:water fraction. Residues in the chloroform fraction and the methanol:chloroform:water fraction (27% of the TRR) were not further characterized. The registrant did not attempt acid, base, or enzyme hydrolysis of the sugar beet leaf/stem fraction.

The methanol:water extract was separated by ion exchange chromatography into neutral, acidic, and basic fractions, as previously described under soybeans. The neutral fraction (11% of the TRR) was not retained on either the cation or anion exchange column. The basic fraction (32% of the TRR) was retained on the cation exchange column. Washing with 6N HCl eluted 22% of the TRR from the cation exchange column. The acidic fraction (20% of the TRR), was retained on the SAX anion exchange column and was not further analyzed.

The neutral and basic sugar beet leaf/stem fractions were analyzed by reverse phase TLC (C-18 plate eluted with methanol:water), normal phase TLC (silica gel eluted with ethyl acetate:i-propanol:water), and by HPLC using a Bio-Rad HPX-87C column with fraction collecting (2 minute fractions) for LSS quantitation. Non-radioactive standards of EU and JB were co-chromatographed to assist in locating the radioactive zones corresponding to those compounds. The radioactive zones on the TLC plates were scraped and counted. The HPLC fractions were counted by LSS. Based on TLC analysis, the methanol:water fraction was reported to contain the following: 0-4% hydantoin; 4% Jaffe's base (JB); 2% ethylene bis isothiocyanate sulfide (EBIS); 8% ethyleneurea (EU); 8% complex carbohydrate; 13% amino acids; and 2% combined ethylene diamine (EDA), 2-imidazoline (IMID), and N-formal EDA. The HPLC analysis reportedly gave similar results. There was no evidence of confirmation of these identifications by a confirmatory method of analysis. The registrant did not explain calculations to permit independent confirmation.

Sugar beet roots. The sugar beet root fraction was serially extracted with water (70% of the TRR), hot water (10% of the TRR), and hot 2M HCl (14% of the TRR). Water extracts were treated with CaO and cleaned-up to remove calcium ion by ion exchange chromatography (Bio-Rad AG-50 column). The CaO treatment precipitated proteins (7% of the TRR). Of the 70% of the TRR extracted with water, 57% eluted from the cation exchange column with water, 23% eluted with 2M HCl, and 23% was retained on the cation exchange column. The CaO precipitate, the hot water and hot 2M HCl extract, and the activity retained on the cation exchange column were not further analyzed. The 2M HCl

eluate was subjected to the ninhydrin test, a qualitative colorimetric test for amino acids and similar functional groups. Based on the positive result, the registrant concluded that amino acids were present. However, some mancozeb degradates also give positive ninhydrin test results. Additionally, the ninhydrin test does not indicate whether the radioactivity is found in amino acids or compounds with similar functional groups.

Water eluates from the water extraction were analyzed by HPLC with two different columns: Bio-Rad HPX-87C, and Erma ERC-N41171 (amino-modified silica gel) with fraction collecting (2 minute fractions) and LSS analysis. The registrant reported that the radioactivity in the extract was distributed as follows: sucrose (36%), glucose (1%), fructose (1%), EU (<3%), and >17% amino acids. However, retention time matching cannot be done, since fraction collecting followed by LSS was done for the radioactivity analyses and a refractive index (RI) detector directly coupled to the HPLC was used for the analysis of non-radioactive standards. We note that retention times of standards of known mancozeb degradates overlap retention times of standards of natural products. For example: (i) hydantoin and the amino acid, ASP, have the same retention time; (ii) EU elutes between the amino acids ALA and VAL; (iii) HYD and ETU elute in a region identified by the registrant as "alcohols, esters?" which have overlapping TLC spots; (iv) the hydantoin TLC spot overlaps sugar spots; (v) ETU and EU have almost the same R_f in reverse phase TLC; (vi) hydantoin and ETU overlap; and (vii) EU and sugars overlap on normal phase TLC. Therefore, the identifications given by the registrant can be considered tentative at best.

The root fraction was also analyzed for sucrose by crystallization of sucrose octaacetate (single crystallization); and for betaine by precipitation of the betaine reineckate complex. Although the crystalline material was analyzed by IR and NMR, and radioactivity was measured in the sucrose octaacetate, the identification of ^{14}C-sucrose must be considered tentative because the precipitate was not recrystallized to constant specific radioactivity.

The distribution and characterization of residues in sugar beet leaf/stem and roots are summarized in Tables 7 and 8.

Table 7. Tentative identification of mancozeb metabolites in sugar beet leaf/stem samples (TRR = 9.5 ppm)[a]

Item	Total radioactive residues %	ppm[b]
Methanol/water extract	(63)	
Neutral fraction	11	1.0
Basic fraction, eluted with 6N HCl	22	2.1
Basic fraction, retained[c]	10	1.0
Acidic fraction[c]	20	1.9
From neutral and basic fractions[d]:		
Hydantoin	2	0.2
JB	4	0.4
EBIS	2	0.2
EU	8	0.8
Complex carbohydrates	8	0.8
Amino acids	13	1.2
EDA + IMID + N-formal EDA	2	0.2
Chloroform extract[c]	10	1.0
Insoluble in methanol/ chloroform/water[e]	(27)	
Hot HCl Extract[c]	16	1.5
Hot methanol extract[c]	4	0.4
Solid remaining[c]	7	0.7
Summary of Tentative Identifications in Sugar Beet Leaf/Stem[f]		
Known degradates[g]	(16)	
Natural Products[h]	(24)	
Not identified/unknown	0-4	
Not analyzed	67	

[a] Identifications are considered tentative because no confirmatory analyses were done.
[b] Residue in ppm mancozeb equivalents.
[c] Not analyzed.
[d] Reported percentage TRR adds up to more than the TRR in the eluates which were analyzed.
[e] Results of further extractions follow in the table.
[f] Identifications are considered tentative because no confirmatory analyses were done. Due to inadequate description of calculations, figures do not add up to 100%.
[g] Identified by TLC R_f, identity not confirmed.
[h] Identified by HPLC fraction.

Table 8. Tentative identification of mancozeb metabolites in sugar beet roots (TRR = 0.5 ppm)[a].

Item	Extract (%)	TRR (%)	TRR ppm[b]
Water extract		(70)	
precipitated by CaO[c]	7	5	0.02
Water extract,			
Not precipitated		(63)	
Retained on AG-50 column[c]	21	13	0.06
Water eluate	57	36	0.18
2M HCl eluate	23	14	0.07
Hot water extract[c]		10	0.05
Hot 2M HCl extract[c]		14	0.07
Solid remaining[c]		6	0.03
From water and 2M HCl eluates[a]			
Sucrose		36	0.18
Glucose		<1	<0.01
Fructose		<1	<0.01
EU		<3	<0.02
Amino acids		>17	>0.09
Summary of Tentative Identifications in Sugar Beets[a]			
Known degradates		(<3)	
Natural components		(55)	
Not analyzed		(48)	

[a] Identifications are considered tentative because no confirmatory analyses were done. Due to inadequate description of calculations, figures do not add up to 100%.
[b] Residues in ppm mancozeb equivalents.
[c] Not analyzed.

Wheat. The Mancozeb Task Force submitted data (MRID 00160703, Rohm and Haas Report No. 31L-86-03; and MRID 00164510, Rohm and Haas Report No. 310-86-54) pertaining to the metabolism of [^{14}C]mancozeb in wheat. Wheat plants were harvested 46 days following the last of three applications of [^{14}C]mancozeb at 2 lb ai/A (14 day intervals). The registered use is a maximum of three applications at 2 lb ai/A with a 26-day PHI. Samples were separated into grain, chaff, and straw. Wheat samples were analyzed for total radioactive residues (TRR) by liquid scintillation spectrometry (LSS) following combustion. The percentage of radioactivity in each plant part was not reported. Samples were also analyzed for CS_2 evolution (mancozeb residues) and for ETU; the results are presented below in Table 9.

Table 9. Residues in wheat seed, chaff, and straw harvested following three applications with [^{14}C]mancozeb.

Item	Residue (ppm mancozeb equivalents)		
	TRR	CS_2	ETU
Seed/Grain	2.4	0.03	<0.007
Chaff	15.8	2.3	<0.007
Straw	23.6	2.1	<0.007

Samples were extracted with either 80% ethanol or methanol:chloroform:water, followed by hot 2N HCl. Residues in the extracts were separated by ion exchange chromatography (as previously described in the soybean and sugar beet metabolism studies) into neutral, basic, and acidic fractions. Bio-Rad AG-50W-X8 cation exchange and Bio-Rad AG-1-X8 anion exchange columns were used. The neutral fraction is not retained by cation or anion exchange columns. The basic fraction is retained by the cation exchange column, but will elute with 6N HCl. The acidic fraction is retained by the anion exchange column but will elute with 6N HCl. Total radioactivity in each of these fractions was reported. Basic fractions were also analyzed by reverse phase and normal phase TLC. Radiolabeled metabolites were visualized by radioautography (as previously described for soybean residues). Neutral fractions were analyzed by HPLC using fraction collection (1-2 minute fractions) and analyzed for radioactivity by LSS. Acidic fractions were not further analyzed. Residues retained by the cation and anion exchange columns which did not elute with 6N HCl were not reported. Results were reportedly similar for the two different solvent systems, and are summarized in a table at the end of this section.

Samples of wheat seed, chaff, and straw were also digested in 6N HCl. The acid digests were concentrated to dryness and reconstituted with water. The solutions were then separated by ion exchange chromatography and analyzed by TLC as described above. The residue remaining after acid digestion was not further analyzed. The distribution and characterization of residues in wheat are summarized in tabular form in Tables 10-13.

In Rohm and Haas Report No. 310-86-54, wheat straw was extracted with ethanol. The extract was not analyzed. The insoluble residue was hydrolyzed with protease to release proteins. The hydrolysate was not analyzed, but was presumed to contain proteins. Following enzyme hydrolysis, the residue was hydrolyzed with 72% sulfuric acid for 2 hours, diluted to 3% sulfuric acid, and refluxed for 4 hours. The supernatant was treated with BaOH, and then fractionated by ion exchange chromatography (as previously described). The neutral fraction was analyzed by HPLC using a Bio-Rad HPX-87C column with fraction collection and analyzed for radioactivity by LSS. The basic fraction was analyzed by HPLC using a Pico-Tag column with eluants A and B and with fraction collection and analyzed for radioactivity by LSS. The residue after treatment with concentrated sulfuric acid was analyzed by IR and elemental analysis. The registrant concluded that the residue was lignin.

Table 10. Tentative identification of mancozeb metabolites in wheat seed (TRR = 2.4 ppm)[a].

Item	Total radioactive residues %	ppm[b]
Ethanol extract	(20)	
Neutral fraction	18	0.4
Basic fraction, eluted with 6N HCl	4	0.1
Basic fraction, retained[c]	NR[d]	NR
Acidic fraction[c]	5	0.1
Acidic fraction, retained[c]	NR	NR
Precipitated during storage (presumed protein)	2	0.05
2N HCl extract	(48)	
Neutral fraction	36	0.9
Basic fraction, eluted with 6N HCl	4	0.1
Basic fraction, retained[c]	NR	NR
Acidic fraction[c]	1	0.02
Acidic fraction, retained[c]	NR	NR
Insoluble in ethanol and 2N HCl[c]	(32)	0.8
From neutral and basic fractions:		
Hydantoin	2	0.05
JB	4	0.1
EBIS	2	0.05
EU	8	0.2
Sugar, amino acids, protein	8	0.3
EDA + IMID + N-formal EDA	2	0.05
Second Extraction Scheme		
6N HCl Extract	(51)	
Amino acids	9	0.2
EDA, JB, amino acids	16	0.4
Not identified	26	0.6
Insoluble in HCl[c]	49	1.2
Summary of Tentative Identifications in Wheat Seed[a]		
Known degradates[e]	(18)	
Natural Products[f]	(9-21)	
Not identified/unknown	(0-26)	
Not analyzed	(49-70)	

[a] Identifications are considered tentative because no confirmatory analyses were done.
[b] Residue in ppm mancozeb equivalents.
[c] Not analyzed.
[d] NR = not reported.
[e] Identified by Reverse phase and Normal phase TLC R_f.
[f] Identified by HPLC, identity not confirmed.

Table 11. Tentative identification of mancozeb metabolites in wheat chaff (TRR = 15.8 ppm)[a]

Item	Total radioactive residues %	Total radioactive residues ppm[b]
Ethanol extract:	(16)	
Neutral fraction	3	0.5
Basic fraction, eluted with 6N HCl	3	0.5
Basic fraction, retained[c]	NR[d]	NR
Acidic fraction[c]	1	0.2
Acidic fraction, retained[c]	NR	NR
2N HCl extract:	(26)	
Neutral fraction	16	2.5
Basic fraction, eluted with 6N HCl	8	1.3
Basic fraction, retained[c]	NR	NR
Acidic fraction[c]	2	0.3
Acidic fraction, retained[c]	NR	NR
Precipitated during storage	2	0.3
Insoluble in ethanol and 2N HCl	(58)	9.2
From neutral and basic fractions[e]:		
Hydantoin	2	0.3
JB	4	0.5
EBIS	2	0.3
EU	8	1.3
Complex carbohydrates	8	1.3
Amino acids	13	2.1
EDA + IMID + N-formal EDA	2	0.3
6N HCl Extract:	(42)	
Amino acids	19	3.0
EDA, JB, amino acids	11	1.7
Not identified	22	3.5
Insoluble[c]	(58)	9.2
Summary of Tentative Identifications in Wheat Chaff[a]		
Known degradates[f]	(18)	
Natural Products[g]	(19-30)	
Not identified/unknown	(0-22)	
Not analyzed	(58-70)	

[a] Identifications are considered tentative because no confirmatory analyses were done. Due to inadequate description of calculations, figures do not add up to 100%.
[b] Residue in ppm mancozeb equivalents.
[c] Not analyzed.
[d] NR = not reported.
[e] Reported percentage TRR adds up to more than the TRR in the eluates which were analyzed.
[f] Identified by Reverse Phase and Normal Phase TLC R_f.
[g] Identified by HPLC, identity not confirmed.

Table 12. Tentative identification of mancozeb metabolites in wheat straw (TRR = 23.6 ppm)[a].

Item	Total radioactive residues %	ppm[b]
First Extraction Scheme		
Ethanol extract	(12)	
Neutral fraction	2	0.5
Basic fraction, eluted with 6N HCl	3	0.7
Acidic fraction[c]	2	0.5
Basic and acidic fractions, retained[c]	NR[d]	NR
Precipitated during storage	1	0.2
2N HCl Extract	(23)	
Neutral fraction	9	2.1
Basic fraction, eluted with 6N HCl	6	1.4
Acidic fraction[c]	2	0.5
Basic and acidic fractions, retained[c]	NR	NR
Insoluble in ethanol and 2N HCl	65	15.3
From neutral and basic fractions[e]:		
Hydantoin	2	0.5
JB	4	0.9
EBIS	2	0.5
EU	8	1.9
Complex carbohydrates	8	1.9
Amino acids	13	3.1
EDA + IMID + N-formal EDA	2	0.5
Second Extraction Scheme		
Ethanol extract[c]	43	10.1
Protease hydrolysate[c]	13	3.1
Concentrated acid extract		
Neutral fraction	2	0.5
Basic fraction, eluted with 6N HCl	6	1.4
Acidic fraction[c]	1	0.2
Basic and acidic fractions, retained[c]	NR	NR
Insoluble in conc. acid (lignin)	23	5.4
Third Extraction Scheme		
6N HCl Extract	(51)	
Amino acids	9	2.1
EDA, JB, amino acids	16	3.7
Not identified	26	6.1
Insoluble[c]	49	11.6

[a] Identifications are considered tentative because no confirmatory analyses were done.
[b] Residue in ppm mancozeb equivalents.
[c] Not analyzed. [d] NR=not reported.
[e] Reported percentage TRR adds up to more than the TRR in the eluates which were analyzed.

Table 13. Summary of tentative identification of mancozeb metabolites in wheat straw (TRR = 23.6 ppm)[a].

Item	Total radioactive residues (%)
Known degradates[b]	(2-16)
Natural products[c]	(>32)
Not identified/unknown	(>0)
Not analyzed	(>56)

[a] Identifications are considered tentative because no confirmatory analyses were done.
[b] Identified by TLC R_f, identity not confirmed.
[c] Identified by HPLC fraction, identity not confirmed.

QUALITATIVE NATURE OF THE RESIDUE IN ANIMALS

Conclusions:

The qualitative nature of the [^{14}C]mancozeb residue in animals is not adequately understood. The Mancozeb Guidance Document, dated 4/87, required additional poultry metabolism studies. The Mancozeb Residue Chemistry Chapter Update No. 1, dated 1/27/87, concluded that the qualitative nature of the residue in poultry is not adequately understood because the submitted studies (MRIDs 00160781 and 00164879) failed to identify ca. 40% of the residue in thigh muscle, 90% of the residue in breast muscle, and 80% of the residue in liver; none of the residue in poultry fat was identified. It was noted that the acid treatments used in the extraction of residues from poultry tissues could result in the hydrolysis of ETU, EU, and IMID to EDA.

Rohm and Haas Company submitted a letter, dated 6/26/87, clarifying the previously submitted poultry metabolism studies and addressing the deficiencies identified in the Residue Chemistry Chapter and Update. The registrant contends that characterization was performed on most fractions containing >10% of the total tissue radioactivity, and that 83-94% of the residues in eggs and tissues were characterized. The registrant also stated that residues in fat were not characterized because analyses for ETU and CS_2-releasing residues consumed all of the available fat sample. The registrant noted that the dosing levels (3,14,and 36 ppm) far exceeded the anticipated exposure level of 0.005 ppm for poultry. Regarding the potential for the hydrolysis of metabolites to EDA during extraction, the registrant stated that strong acid and buffered protease released similar amounts of radioactivity, but that due to concerns about acid hydrolysis, metabolite characterization was carried out primarily with protease hydrolysates.

After reexamining the poultry metabolism data, we conclude that the requirements for additional data remain outstanding. Only ca. 30-50% of the TRR in eggs and tissues was identified, and most of those identifications are considered tentative due to poor separation of metabolites on TLC or the failure to perform confirmatory analyses. In eggs, the only metabolites with verified identities were ETU (up to 7% of the TRR) and glycine (maximum of 10%; uncertain due to the co-migration of EDA with underivatized glycine on TLC). In liver, the presence of ETU was confirmed (<1% of the TRR), as were NAcEDA (1%) and EDA (percentage undetermined due to co-migration of glycine with EDA). See Table 1 for the full chemical names of tentatively identified metabolites. We do not consider unanalyzed fractions from ion exchange chromatography or radioactivity at the origin of TLC plates to be sufficiently identified. Additionally, our most recent calculations for the maximum dietary burden in poultry was 11 ppm (S. Hummel memo of 7/13/88, RCB No. 2966), considerably higher than the registrant's estimate of 0.005 ppm. The following data are required:

- Data depicting the metabolism of [^{14}C]mancozeb in poultry. The submitted studies on laying hens (MRIDs 00160781 and 00164879) are potentially upgradeable. Additional data are required depicting the characterization and identification of residues in eggs and tissues. Only ca. 30-50% of the TRR in eggs and tissues were characterized. The unanalyzed fractions from ion exchange chromatography and radioactivity at the origin of TLC plates were not sufficiently identified. The identification of residues is considered tentative due to poor separation of metabolites on TLC or the failure to perform confirmatory analyses. In eggs, the only metabolites with verified identities were ETU (up to 7% of the TRR) and glycine (maximum of 10%; uncertain due to the co-migration of EDA with non-derivatized glycine on TLC). In liver, the presence of ETU was confirmed (<1% of the TRR), as were NAcEDA (1%) and EDA (percentage undetermined due to co-migration of glycine with EDA). Representative samples from these studies must be analyzed by the residues analytical methods developed for data collection and tolerance enforcement to ascertain that these methods are capable of adequately recovering all metabolites of concern.

The interpretation of Agency guidelines regarding metabolism studies have become stricter and therefore, the available and previously submitted ruminant metabolism studies (MRIDs 00160780 and 00164880) have been reevaluated. Based on current Agency policy, we conclude that the nature of the residue in ruminants is not adequately understood for the following reasons: (i) the

only metabolite for which identity was confirmed was ETU, accounting for 5.2-28.6% of the TRR in milk, 0.5-1.3% of the TRR in liver, 1.9-2.6% in kidney, and 3.7-10.5% in muscle; (ii) metabolite identifications other than ETU are considered tentative because TLC resolution was poor and/or no confirmatory analyses were performed; and (iii) evidence for the presence of radioactivity in natural products was inconclusive and the levels of ^{14}C-activity in these components were quite variable. In addition, the maximum dosing level, equivalent to 36 ppm in the diet, may not adequately represent the theoretical dietary burden for dairy animals. The following additional data are required:

- Data depicting the metabolism of [^{14}C]mancozeb in ruminants. The submitted study on lactating goats (MRIDs 00160780 and 00164880) is potentially upgradeable. Additional data are required depicting the characterization and identification of residues in fat. The identity of metabolites, other than ETU, in tissues and milk is considered tentative because TLC resolution was poor and no confirmatory analyses were performed. The evidence for the presence of radioactivity in natural products was inconclusive since the levels of ^{14}C-activity in these components was quite variable. Representative samples from these studies must be analyzed by the residue analytical methods developed for data collection and tolerance enforcement to ascertain that these methods are capable of adequately recovering all metabolites of concern.

References (used):

MRID(s): 00160780. 00160781. 00164879. 00164880.

Discussion of the data:

Metabolism studies on goats (MRIDs 00160780 and 00164880) and laying hens (MRIDs 00160781 and 00164879) have been previously submitted and evaluated in the Residue Chemistry Chapter of the Mancozeb Registration Standard, dated 9/86, and the Mancozeb Update No. 1, dated 1/87. These data are resummarized here for clarity and continuity and are reevaluated with respect to their adequacy in meeting current Agency requirements. It should be noted that in recent years, Agency interpretation of existing regulations has become stricter, and that conclusions reached previously may be modified in this review.

Metabolism in Lactating Goats. The fractionation and characterization of ^{14}C-residues in milk and initial analyses of muscle and liver were previously reported in MRID 00160780 (1986; Report No. 31L-86-40). The analysis of residues in kidney and additional data pertaining to the characterization of bound residues and radioactivity of natural products in tissues were previously reported in MRID 00164880.

Lactating goats were orally dosed with [^{14}C]mancozeb, once daily for 7 days via capsule at a rate equivalent to 3, 14, or 36 ppm in the diet. Milk was collected twice daily and pooled into a single daily sample; urine and feces were collected daily. The goats were sacrificed 24 hours after the final dose and samples of muscle, kidney, liver, heart, gall bladder, and blood were collected. Total radioactive residues (TRR) in tissue and feces samples were determined by liquid scintillation spectrometry (LSS) following combustion. Milk and urine were analyzed directly by LSS. The total radioactive residues in tissues, milk, urine, and feces, and an accounting for the administered radioactivity are summarized in Table 14.

Table 14. Total radioactive residues (ppm mancozeb equivalents) in tissues from goats dosed with [^{14}C]mancozeb at dietary levels of 3, 14, and 36 ppm.

Tissue	Dosing level[a]					
	3 ppm		14 ppm		36 ppm	
Feces	3.02	(50)	10.08	(47)	28.4	(41)
Urine	0.82	(31)	1.65	(32)	8.34	(34)
Milk	0.046	(0.17)	0.18	(0.7)	0.9	(1.46)
Muscle						
longissimus dorsi	0.041	(0.04)	0.11	(0.02)	0.55	(0.05)
semimembranous	0.045	(0.05)	0.14	(0.03)	0.66	(0.05)
triceps	0.045	(0.04)	0.13	(0.02)	0.6	(0.04)
others	0.044	(0.95)	0.13	(0.53)	0.6	(1.1)
Fat						
omental	0.016	(0.06)	0.026	(0.02)	0.09	(0.03)
perirenal	0.026	(0.02)	0.023	(0.01)	0.13	(0.02)
other	0.021	(0.25)	0.025	(0.05)	0.11	(0.11)
Heart	0.042	(0.02)	0.16	(0.02)	0.68	(0.03)
Kidney	0.21	(0.07)	0.58	(0.04)	2.84	(0.09)
Liver	0.82	(1.65)	2.11	(0.85)	6.23	(0.99)
Gall bladder	0.32	(0.07)	0.6	(0.01)	1.28	(0.01)
Blood	0.061	(0.31)	0.24	(0.23)	0.85	(0.37)
Total % Recovered		(85.7)		(81.53)		(79.35)

[a] The percentages of the total dosed radioactivity are given in parentheses.

The total radioactive residues in milk from the high-dose (36 ppm) group were 0.16 ppm on day 1, increasing to a plateau level of 0.97-0.99 ppm which was maintained in samples collected on days 5 through 7.

Extraction

Residues in milk were extracted with acetonitrile and the extract centrifuged to collect precipitated proteins and lipids. The percent distribution of total radioactivity in fractions of milk collected on day 7 is presented in Table 15. The protein fraction from the acetonitrile precipitation was dialyzed with a membrane having a molecular weight (MW) cutoff of 8,000 and samples of the dialysate and retentates were removed for radioanalysis. Gel permeation chromatography (GPC) with BioGel P-30 permeation column (3000-45000 dalton fraction range) separated the protein fraction into two unidentified peaks. Eluates were analyzed for radioactivity by LSS. The major peak (75% of the applied radioactivity) eluted shortly after the void volume of the column and the minor peak (24%) eluted as a lower molecular weight species. These peaks were not identified; the registrant stated that the major proteins in milk are casein (MW 23,600), lactoglobulin (MW 35,000), and lactoalbumin (MW 17,000). Lipids were extracted from the precipitate and the acetonitrile extract using hexane. The lipid fraction (hexane-soluble) was saponified, hexane partitioned, and the released fatty acids were derivatized to the methyl ester (using methanol and boron trifluoride as a promotor). Following partitioning by petroleum ether, the fatty acid esters were assayed using TLC on silica gel plates developed with unspecified solvent systems; TLC analyses separated two bands containing saturated fatty acids and mono-enoic fatty acids. Radioactive metabolites were visualized by radioautography and quantified by scraping radioactive spots into vials containing Oxosol followed by LSS analysis. Non-radioactive standards were visualized using the following specific colorimetric spray reagents:

(i) 0.5% *p*-dimethyl-aminocinnamaldehyde in ethanol:4N hydrochloric acid (3:1, v:v) (for EBIS, ETU, EU, and Jaffe's Base);

(ii) Gibb's Reagent; 0.5% 2,6-dichloroquinone-4-chlorimide in ethanol (for N-acetylethylenediamine, EBIS, EDA, ETU, N-formylglycine, glycine, IMD, and Jaffe's Base);

(iii) FN Reagent; 10% sodium hydroxide:10% sodium nitroferricyanide:10%potassium ferricyanide:water (1:1:1:3, v:v:v:v) (for EBIS, ETU, EU, and hydantoin); and

(iv) 0.5% Fluorescamine in acetone (for N-acetylethylene-diamine, EDA, and glycine).

Residues in the aqueous acetonitrile fraction were extracted with ethyl acetate. Ethanol was added to the aqueous fraction to precipitate lactose. Lactose was derivatized by acetylation, then separated on TLC silica gel (unspecified solvent) by co-chromatography. The acetonitrile:ethyl acetate and aqueous ethanol fractions were also analyzed using TLC on silica gel plates developed with one of three different solvent systems: (i) ethylacetate:2-propanol:water (65:25:10, v:v:v:; system A); (ii) absolute ethanol:ethyl acetate:ammonium hydroxide (3:1:1, v:v:v; system B); or (iii) absolute ethanol:ammonium hydroxide (4:1, v:v; system C). Degradates were visualized using radioautography and the four colorimetric spray reagents described above.

Table 15. Percent distribution of total radioactivity in fractions of milk collected on day 7.

Fraction	Dose level (ppm)		
	3	14	36
Acetonitrile-soluble (protein)	23.5	27.5	29.4
Hexane-soluble (lipid)	9.4	4.4	16.9
Ethanol-insoluble (lactose)	7.3	6.3	10.4
Ethyl acetate:acetonitrile	-	-	28.2
Aqueous ethanol	59.8[a]	61.8[a]	15.1

[a] The value reported is for the combined ethyl acetate:acetonitrile and aqueous ethanol fractions.

Residues in muscle, liver, and kidney were extracted five times in a tissue homogenizer at 10,000 rpm with methanol:chloroform:water (11:5:5, v:v) and the solids separated from the extract by centrifugation. When the successive extracts were combined, the alcohol content increased (early extracts were enriched with water from the tissue), causing material (thought to be glycogen) to precipitate. An equal volume of chloroform was added to the extract and the chloroform-rich phase was separated by centrifugation; this solution was reduced to an oily residue and tentatively identified as lipids without further analysis. All fractions were radioassayed using LSS. The aqueous fraction was concentrated and mixed with absolute ethanol and the resulting precipitate, (thought to consist of creatines, creatinines, and bile salts) was sedimented by centrifugation. Aliquots of the aqueous supernatant was analyzed using TLC in silica gel plate developed with solvent systems A and B, described above. Radioactive metabolites were visualized and quantified by radioautography and LSS as previously described. Non-radioactive standards were visualized using previously described colorimetric spray reagents.

Non-extractable residues from tissues were digested in a nonspecific protease enzyme (Pronase E, Type XIV; Sigma Corp.) at 7.5 pH and at room temperature for 24 hours; undigested material was separated by centrifugation. The solubilized residues were radioassayed and analyzed using TLC, both as the dansyl derivatives and as underivatized residues. Dansyl derivatives of amine-containing ^{14}C-residues were prepared by mixing dansyl chloride with the extract in triethylamine or sodium bicarbonate at 80 C for 1 hour; derivatized residues were analyzed using TLC on silica gel plates developed with chloroform:methanol:ethyl acetate:acetic acid (30:20:50:1, v:v:v:v; solvent E). Non-derivatized residues were analyzed using TLC on silica gel plates developed with solvent system B, as described above. Radioactive metabolites were visualized and quantified by radioautography and LSS as previously described. Non-radioactive standards were visualized using previously described colorimetric reagents.

Characterization of metabolites

TLC analyses of ^{14}C-residues in extracts of milk and tissues, suggested the existence of several metabolites of mancozeb. However, the identities and quantities of these metabolites are considered tentative because some of the compounds were not well separated from one another in the solvent systems used and only ETU was subjected to verification using additional methodology.

A component designated "unknown #1" accounted for up to 21% of the total ^{14}C-residue in tissues and 32% in urine. To isolate the compound from urine, the sample was cleaned up on a Sep-Pak silica cartridge eluted with ethyl acetate and methanol. The methanol fraction was analyzed using TLC on silica gel plates using solvent system B. The radioactive areas were visualized by radioautography; the radioactive zones were scraped from the plate and eluted with methanol:water (1:1, v:v). The eluate concentrated and re-chromatographed using solvent system E, and the resulting radioactive residues were analyzed using HPLC with a C-18 reverse phase column, mobile phase of 0.2N sodium phosphate (pH 2), with a flow-through radioactivity monitor and a UV detector (240 nm). The radioactive metabolite exhibited a similar elution pattern from HPLC as standard allantoin, identified as a urinary metabolite in previous studies. Since the compound from urine co-chromatographed with "unknown #1" from tissue extracts, it was concluded that the unknown metabolite is allantoin. Confirmatory analyses were not conducted but are needed since the unknown was not clearly resolved from all other metabolites.

Approximately 60-80% of the nonextractable radioactivity was rendered soluble following protease digestion. Amine-containing, radioactive residues were derivatized with 1 ppm dansyl chloride in acetone with triethylamine or sodium bicarbonate to form fluorescent derivatives. Dansylated residues were separated

using TLC on silica gel plates developed with ethyl acetate:methanol (9:1, v:v). Visualization methods used to identify dansylated derivatives were not presented, but all metabolites were visualized by radioautography. The TLC analysis resulted in the isolation of seven radioactive components which were also reactive to dansyl chloride. Individual amino acids were not identified and the co-migration of other metabolites of mancozeb with dansylated amino acids could not be ruled out.

The identity of glycogen as the ^{14}C-residue precipitated by alcohol during tissue extraction was supported by the observation that standard glycogen behaved the same when subjected to the extraction procedure used for tissues. The results of dialysis indicated that ca. 67% of the radioactivity was in a fraction representing molecular weights <8,000 daltons; the report stated that low molecular weight glycogen would be expected due to physical shearing of the molecules during processing. No further characterization of this fraction was conducted.

The fraction from tissues thought to consist of creatines were analyzed using TLC on silica gel plates developed with 2-propanol:acetone:ammonium hydroxide:water (5:2:4:1, (v:v:v:v). Zones containing isolated creatines were visualized colorimetrically using 2,3-butanedione and alkaline 1-naphthol, a reagent that does not react with the known mancozeb degradates. Radioactive zones were scraped off the plates and analyzed by LSS. The results were reported only for tissues from the animal dosed at 14 ppm; creatine, creatine phosphate, creatinine, and phosphocreatine were identified, although whether identification was based on co-chromatography or comparison with known R_f values was unclear. Unknown polar compounds accounted for 13-18% of the creatine fractions and nonpolar unknowns accounted for 4-15%; <3% of the TRR in the tissues was in unknown creatines.

Tentative identification of ^{14}C-residues in milk collected on day 7 and in tissues is summarized in Tables 16-20. It should be noted that the concentrations of metabolites are expressed in ppm based on the estimated specific activity of the components as derived from ethylene-labeled [^{14}C]mancozeb, not as mancozeb equivalents.

Table 16. Tentative identification of ^{14}C-residues in milk from goats administered [^{14}C]mancozeb in the diet, expressed as percent of the TRR and as ppm, based on the estimated specific activity of the component as derived from [^{14}C]mancozeb.

	Dose level					
	3 ppm		14 ppm		36 ppm	
Component	%	ppm	%	ppm	%	ppm
Extractable[a]						
EDA	2.4	0.003	13.4	0.006	3.8	0.005
N-f-gly	17.7	0.003	10.2	0.007	19.6	0.065
N-ac-EDA	3.5	0.001	6.8	0.005	6.5	0.02
EU	5.2	0.001	10.0	0.006	8.2	0.02
ETU	28.6	0.005	13.0	0.009	5.2	0.015
TLC unknown	2.4	--	8.4	--	0.0	--
Total	59.8		61.8		43.3	
Protein	23.5	--	27.5	--	29.4	--
Lactose	7.3	--	6.3	--	10.4	--
Lipid	9.4	--	4.4	--	16.9	--

Summary of tentative residue characterization in milk:

Known mancozeb degradates	40.5-57.4%
Putative natural components	(38.2-57.4%)
Protein	23.5-29.4%
Lactose	6.3-10.4%
Lipid	4.4-16.9%

[a] Degradates of mancozeb were tentatively identified using TLC analysis of the ethyl acetate:acetonitrile and/or aqueous ethanol extracts; recovery of radioactivity from TLC was not reported and, therefore, the percentages are based on 100% recovery.

Table 17. Tentative characterization of ^{14}C-residues in tissues of goats administered [^{14}C]mancozeb at a level equivalent to 3 ppm in the diet.

Fraction/ Component	Liver		Kidney	
	% of TRR	ppm	% of TRR	ppm
Lipids	1.7		4.6	
Glycogen	3.3		3.7	
Creatines	16.3		6.5	
Aqueous ethanol	(33.7)[a]		(37.4)	
Gly	5.2	0.012	6.6	0.004
N-f-gly	1.6	0.002	2.0	0.002
EDA	-		1.9	0.001
N-ac-EDA	2.1	0.006	1.4	0.001
EU	0.6	0.002	2.4	0.002
ETU	0.5	0.002	1.9	0.001
Hydantoin	0.2	0.001	1.4	0.001
EBIS	0.3	0.001	0.3	0.001
Allantoin	21.1		14.7	
TLC unknown	1.7		1.8	
Sub-total	33.3		34.4	
Hydrolyzed solid residue				
Amino acids	35.3		27.8	
Unextractable	9.5		6.0	
Sub-total	44.8		33.8	
Total recovery (%)	99.4		83.0	

[a] The values in parentheses indicate the percentage of the TRR extracted into aqueous ethanol.

Table 18. Tentative characterization of ^{14}C-residues in tissues of goats administered [^{14}C]mancozeb at a level equivalent to 14 ppm in the diet.

Fraction/ Component	Liver		Kidney		Muscle	
	%	ppm	%	ppm	%	ppm
Lipids	2.7		4.2		3.7	
Glycogen	2.6		8.0		0.1	
Creatines	13.1		9.0		8.5	
Aqueous ethanol	(37.5)[a]		(29.5)		(45.9)	
Gly	4.5	0.029	7.8	0.013	3.9	0.002
N-f-gly	1.5	0.021	2.0	0.005	1.8	0.001
EDA	--[b]		1.6	0.002	--	
N-ac-EDA	2.2	0.020	3.7	0.009	3.1	0.002
EU	1.1	0.008	1.9	0.004	4.8	0.002
ETU	0.9	0.008	1.1	0.003	4.0	0.003
Hydantoin	0.9	0.007	4.1	0.003	3.7	0.002
EBIS	0.4	0.001	0.3	0.001	0.4	0.001
Allantoin	16.3		6.5		11.2	
TLC unknown	--		1.4		3.9	
Sub-total	27.8		30.4		36.8	
Solid residue						
Amino acids	32.2		31.2		32.2	
Unextractable	13.7		15.3		9.6	
Sub-total	45.9		46.5		41.8	
Total recovery	92.1		98.1		90.9	

[a] The values in parentheses indicate the percentage of the TRR extracted into aqueous ethanol.
[b] Indicates none detected.

Table 19. Tentative characterization of ^{14}C-residues in tissues of goats administered [^{14}C]mancozeb at a level equivalent to 36 ppm in the diet.

Fraction Component[a]	Liver		Kidney		Muscle	
	%	ppm	%	ppm	%	ppm
Lipids	4.9		8.5		7.9	
Glycogen	1.6		6.8		0.5	
Creatines	9.9		5.2		14.5	
Aqueous ethanol	(19.5)		(29.2)		(44.3)	
Gly	2.5	0.065	7.7	0.068	5.3	0.009
N-f-gly	0.6	0.021	3.2	0.038	3.2	0.008
N-ac-EDA	0.9	0.033	1.4	0.017	3.7	0.009
EU	1.3	0.040	1.4	0.014	2.5	0.005
ETU	1.3	0.026	2.6	0.031	10.5	0.025
Hydantoin	0.3	0.010	0.5	0.006	2.1	0.005
EBIS	0.2	0.012	0.2	0.005	0.2	0.001
Allantoin	8.0		9.6		5.8	
TLC unknown	1.4		0.9		3.5	
Sub-total	16.5		27.5		36.8	
Hydrolyzed solid residue						
Amino acids	59.1		26.7		27.3	
Bound residue	7.0		13.1		5.6	
Sub-total	58.9		39.8		32.9	
Total recovery	**91.8**		**87.8**		**92.6**	

[a] The values in parentheses indicate the percentage of the TRR extracted into aqueous ethanol.

Table 20. Summary of tentative residue characterization in goat tissues.

Fraction/ Component	Percent of the TRR		
	Liver	Kidney	Muscle
Identified mancozeb metabolites[a]	15.1-31.6	26.4-32.6	32.9-33.3
Natural components	(50.6-75.5)	(38.0-52.4)	(44.4-50.2)
Amino acids	32.2-59.1	26.7-31.2	27.3-32.2
Glycogen	1.6-3.3	3.7-8.0	0.1-0.5
Creatines	9.9-16.3	5.2-9.0	8.5-14.5
Lipids	1.7-4.9	4.2-8.5	3.7-7.9
Unidentified[b]	8.4-13.7	7.9-16.7	9.1-13.5
Losses	0.6-8.2	4.9-17.0	7.4-9.1

[a] Includes "unknown #1" present in the metabolite extracts and tentatively identified in urine as allantoin.
[b] Includes fractions unanalyzed.

Enforcement Analytical Method - Mancozeb and ETU

Muscle and liver tissues were analyzed for mancozeb, and ETU and milk was analyzed for ETU using currently available enforcement methods. Data depicting residues of mancozeb were analyzed using a gas chromatography method (modified by Keppel) with sulfur specific flame photometric detection (GC/FPD-S) with a limit of detection of 0.05 ppm and residues of ETU were analyzed using a GLC/FPD method (Haines and Adler). Residues of mancozeb were 0.21 ppm in liver and 0.3 ppm in muscle. Residues of ETU were 0.04 ppm in liver, 0.04 ppm in muscle, and 0.012 ppm in milk (day 7 sample). No data were submitted depicting mancozeb in milk, kidney, or fat and no data were submitted depicting ETU in kidney or fat. The registrant must submit data depicting the ability of the enforcement methods to detect mancozeb, ETU, and any other residues of concern in tissues of muscle, kidney, liver, fat, and milk.

Following reevaluation of the available data on ruminant metabolism, we conclude that the nature of the residue in ruminants is not adequately understood for the following reasons: (i) the only metabolite for which identity was confirmed was ETU, accounting for 5.2-28.6% of the TRR in milk, 0.5-1.3% of the TRR in liver, 1.9-2.6% in kidney, and 3.7-10.5% in muscle; (ii) metabolite identifications other than ETU are considered tentative because TLC resolution was poor and/or no confirmatory analyses were performed; (iii) evidence for the presence of radioactivity in natural products was inconclusive and the levels of ^{14}C-activity in these components was quite variable; and (iv) the maximum dosing level, equivalent to 36 ppm in the diet, may

not adequately represent the maximum theoretical dietary burden for dairy animals.

Metabolism in Laying Hens: Rohm and Haas Company submitted data (MRID 00160781) pertaining to the metabolism of mancozeb in white Leghorn laying hens. Twenty-five hens (5 groups; 5 hens/group) received oral capsular doses of [^{14}C]mancozeb for 7 consecutive days at a level equivalent to ca. 0, 3, 14, and 36 ppm in the diet. Eggs were collected daily, pooled by treatment groups, blended, and subsampled. Excreta from all dose groups were collected, pooled by treatment group, blended with water, and subsampled. The hens were sacrificed 24 hours after the final dose. Breast and thigh muscles, fat, liver, kidney, gizzard, and heart samples were collected, pooled by treatment groups, and homogenized. The total radioactivity in soluble samples, extracts, and unextractable residues in excreta, eggs and tissue samples were quantified either directly by liquid scintillation spectrometry (LSS) or following combustion (solid samples).

Total Radioactive Residues

The total radioactive residue (TRR) or ^{14}C-activity in soluble samples, extracts, and unextractable residues showed that 88.2% of the administered ^{14}C-activity was recovered in excreta, eggs, and tissues of the dosed hens (36 ppm dose group). The excreta, eggs, and tissues of hens dosed at 36 ppm contained 87.4%, 0.46% and 0.35%, respectively, of the recovered ^{14}C-activity. The highest concentrations of [^{14}C]mancozeb residues in the tissues of 1.92 and 1.98 ppm were found in liver and kidney, respectively. The level of ^{14}C-residues level in eggs from hens dosed at 36 ppm increased steadily from 0.025 ppm on the first day of sampling to a peak of 0.849 ppm on day 7 of sampling; residues in eggs from the 14 ppm dose group increased from 0.0088 ppm on day 1 to 0.261 ppm on day 7. Eggs from the low (3 ppm) dosed hens increased from 0.0197 ppm on day 2 to 0.0498 ppm on day 7; samples collected on days 3 and 6 bore residues below the limit of detection (<0.001 ppm). The summarized data are presented in Table 21. All analytical data were obtained from egg and tissue samples of the dose group hens administered 36 ppm of mancozeb.

Table 21. Percent distribution of recovered ^{14}C-activity in excreta, eggs, and tissues of hens dosed with [^{14}C]mancozeb at 3 to 36 ppm.

	Dosing level					
	3 ppm		14 ppm		36 ppm	
Tissue	%	ppm	%	ppm	%	ppm
Excreta	82.8	4.77	81.9	47.4	87.4	84.4
Whole Egg	0.193	0.05	0.376	0.260	0.463	0.849
Breast Muscle	0.0166	0.0105	0.0209	0.065	0.029	0.224
Thigh Muscle	0.0226	0.0142	0.0273	0.0846	0.0384	0.295
Kidney	0.0465	0.146	0.0515	0.747	0.0545	1.98
Liver	0.0888	0.097	0.134	0.692	0.138	1.92
Heart	0.0051	0.027	0.0055	0.146	0.006	0.429
Gizzard	0.0448	0.073	0.0836	0.662	0.0761	1.46
Fat	0.0016	0.008	0.005	0.064	0.005	0.237
Total	83.3		82.6		88.2	

Extraction

Excreta, egg, and tissue samples were solvent extracted. Each extraction consisted of solvent addition, homogenization, centrifugation, separation, and radioanalysis. Unextractable residues were combusted and radioassayed. Portions of the unextractable residues from egg and tissue samples were digested in 6N HCl.

Kidney samples were extracted with methanol:chloroform:water (11:55:5, v:v:v), methanol, water, and hexane. About 27% of the total ^{14}C-activity in kidney samples was extractable. A portion of the combined methanol:chloroform:water extracts was radioassayed and the remainder partitioned with chloroform:water (32:5, v:v). The aqueous methanol layer was removed from the semi-solid methanol:chloroform interface. Most of the ^{14}C-activity partitioned into the aqueous methanol layer. Chloroform-soluble residues were re-extracted with 60% methanol and the aqueous methanol extracts were pooled and filtered to remove traces of suspended solids. The aqueous methanol layer was fractionated into neutral, basic, and acidic fractions. The neutral and basic fractions were analyzed using TLC on silica gel plates developed with ethyl acetate:2-propanol:water (65:25:10 or 3:1:1, v:v:v; solvent system A) and 2-propanol:ammonium hydroxide (4:1, v:v; solvent system B). A major unknown was isolated and re-chromatographed using TLC on silica gel plates developed with chloroform:ethyl acetate:methanol:2N ammonium hydroxide (3:5:3:1, v:v:v:v) and ethyl acetate:water:acetone (3:1:1, v:v:v). The unknown metabolite did not co-chromatograph with any known mancozeb metabolite. Metabolites were visualized by

radioautography, UV-light, fluorescence, and/or the following colorimetric spray reagents: (i) FN Reagent (for EBIS, ETU, hydantoin, Jaffe's Base, and IMD); (ii) Erhlich's Reagent (for EU); and (iii) Fluorescamine (for N-acetylethylene-diamine, EDA, and glycine).

The sample of whole egg was extracted similarly but without methanol extraction and only chloroform was added to the combined methanol:chloroform:water extracts.

Thigh muscle samples were extracted with hexane, methanol, and water. The combined aqueous methanol extracts were partitioned with chloroform. The aqueous layer was removed, filtered, and separated into neutral, basic, and acidic fractions by ion exchange chromatography. The neutral fraction was analyzed using TLC on silica gel plates developed 2-propanol:ammonium hydroxide (4:1, v:v). Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS. About 65% of the ^{14}C-activity in thigh muscle tissue was solvent extractable.

Breast muscle samples were extracted with methanol:chloroform:water (11:5:5, v:v:v), chloroform:methanol (2:1, v:v), methanol, and water. The methanol and chloroform:water extracts were combined and partitioned with chloroform. The aqueous layer was removed, filtered, and fractionated by ion exchange chromatography. The neutral fraction was analyzed using TLC on silica gel plates developed with solvent systems A and B as previously described. Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS.

Liver samples were sequentially extracted with methanol:chloroform:water (11:5:5, v:v:v), methanol:chloroform (11:55,v:v), chloroform:methanol (2:1, v:v), methanol, and water. The methanol:chloroform:water extracts were combined. A portion of the combined extracts was radioassayed and the remainder was combined with chloroform:water (7:1, v:v). The aqueous methanol layer was decanted and allowed to separate into water and methanol fractions. The fractions were dried, suspended with water and methanol, respectively, and analyzed using TLC developed with solvent systems A and B. Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS.

The unextractable residues from eggs and tissues were digested in 6N hydrochloric acid at 110 C for 18-24 hours and the hydrolysates were filtered. The filtrates were concentrated by evaporation and radioassayed. The acid hydrolysates were fractionated by ion exchange chromatography; basic and neutral fractions (breast, thigh, and kidney eluates), and basic

fractions (liver eluates) were analyzed using TLC as earlier described. Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS. About 83-92% of the total ^{14}C-activity in solvent unextractable egg and tissues residues was hydrolyzed by protease and/or acid. Approximately 3-7% of the total activities in eggs and tissues were not hydrolyzable.

Protease-digested residues in liver and eggs were reacted with dansyl chloride. The mixtures were extracted with toluene to remove didansyl ethylenedithiourea and didansyl N-actyl ethylenedithiourea leaving dansylated amino acids in the aqueous phases. The toluene and aqueous phases were analyzed using TLC (details not provided).

Characterization/Identification

Fractionated and unfractionated solvent extracts and acid hydrolysates of the ^{14}C-residues in egg and tissues were analyzed by co-migration with known unlabeled mancozeb degradation products on TLC plates. The metabolites in solvent extracts and acid hydrolysates were separated and tentatively identified using TLC on silica gel plates developed with the solvent systems described above (see "Extraction" section) for each tissue. The ^{14}C-residues in egg and tissue extracts were tentatively identified as ethylenebisthiocarbamate (EBIS), ethylenethiourea (ETU), hydantoin (HYD), 2-imidazoline (IMID), ethylenediamine (EDA), N-acetyl ethylenediamine (N-AcEDA), ethyleneurea (EU), and Jaffe's Base (JB). EBDC residues and metabolites in eggs and tissues also were analyzed using GC on a Tenax GC column and quantified using a flame photometric detector (FPD) in the sulfur specific mode. Residues of EBDC were decomposed to CS_2 gas following acid hydrolysis of tissue and egg samples; the CS_2 gas was trapped in ethanol on dry ice prior to analysis. Confirmatory analysis of EBDC residues was conducted by analyzing an aliquot of the CS_2-containing ethanol using GC/MS under operating conditions identical to the EBDC GC/FPD method. The ionization source for MS was unspecified. ETU residues in eggs and tissues were analyzed by GC/FPD on a 10% Carbowax 20M/2% KOH column. Prior to GC/FPD analysis, ETU residues were converted to their *S*-butyl derivatives with bromobutane in the presence of dimethylformamide and sodium borohydride. Confirmatory analysis of ETU residues was conducted by analyzing an aliquot of the derivatized residues extracted from eggs and tissues by GC/MS under operating conditions identical to the ETU GC/FPD method.

Summaries of the patterns of residue extraction from eggs and tissues and tentative identifications mancozeb metabolites are presented in Tables 22-27.

Table 22. Distribution of radioactivity in eggs from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 0.849 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
First extraction:		
Methanol/water	(40.2%; analyzed using TLC)	
EBIS	0.12	0.001
ETU	6.8	0.058
EU	20.3	0.172
EDA/GLY	1.5	0.013
NAcEDA	3.1	0.026
Origin/unknown	8.3	0.070
Chloroform	5.0	
Methanol	5.0	
Water	4.4	
Hexane	1.1	
Unextracted	44.2	
Second extraction:		
Methanol/water	(34.1%; analyzed using TLC)	
ETU	0.72	0.006
EU	21.2	0.180
JB	0.68	0.006
NAcEDA	0.72	0.006
HYD	1.64	0.014
EDA/GLY	1.57	0.013
Origin	4.71	0.040
Chloroform	(21.2%; analyzed using TLC)	
EBIS	0.19	0.002
ETU	1.46	0.012
EU	8.06	0.068
NAcEDA	0.23	0.002
HYD	0.42	0.004
EDA/GLY	1.8	0.015
Origin	2.5	0.021
Water	3.4	
Hexane	4.3	
Unextracted	(33.4)	
Acid hydrolyzed	33.0	
ETU/JB	0.3	0.003
EU	0.7	0.006
HYD	0.87	0.007
IMID	1.97	0.017
EDA/GLY	8.98	0.076
Origin	8.15	
Dansylated protease hydrolysate		
Dansyl gly	2.1	0.018
Dansyl amino acids	6.1	0.052

Table 23. Distribution of radioactivity in fractions of thigh muscle from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 0.295 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
First extraction		
Methanol/Aqueous	(48.1%)	
Neutral	(31.0%; analyzed using TLC)	
EU	13.9	0.04
N-AcEDA	1.0	0.003
EDA/GLY	2.8	0.008
HYD	0.7	0.002
IMID	1.9	0.006
Origin/unknown	10.8	
Basic	14.4	
Acidic	4.2	
Chloroform (lipid)	2.9	
Hexane (lipid)	0.8	
Water	5.2	
Unextracted	(39.1)	
Acid hydrolyzed	30.9	
Second extraction		
Methanol	50.5	
Water	4.4	
Hexane	0.5	
Unextracted	(44.6)	
Protease hydrolyzed	(37.2)	
Basic fraction	(31.7; analyzed using TLC)	
EU	1.5	0.004
N-AcEDA	3.3	0.015
EDA/GLY	9.9	0.029
HYD	4.2	0.012
Origin/unknown	5.4	
Neutral fraction	3.6	
Unhydrolyzed	7.4	

Table 24. Distribution of radioactivity in fractions of breast muscle from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 0.224 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
First extraction		
Methanol/ aqueous	(55.7%)	
Neutral	(36.4%; analyzed using TLC)	
EU	35.9	0.08
Basic	15.0	
Acidic	1.0	
Chloroform (lipid)	5.1	
Water	1.5	
Chloroform/methanol	1.5	
Unextracted	(35.3%)	
Acid solubilized	(36.0)	
Basic	26.9	
acidic	0.8	
neutral	0.4	
Acid insoluble	0.0	
Second extraction		
Methanol:chloroform:water	57.6	
Water	1.2	
Unextracted	(41.1%)	
Protease digested	(34.4)	
Basic	(28.6%; analyzed using TLC)	
EU	1.1	0.002
EDA/GLY	9.87	0.022
Origin/unknown	18.36	
Other	2.8	
Undigested	6.7	
Neutral/acid	1.2	

Due to dissimilarities in the first and second extractions, estimates of identified bound and free metabolites and uncharacterized fractions were not made. EU (35.9% of the TRR), was the only free metabolite identified in the first extraction; based on data from the second extraction, bound EU could account for an additional 1% of the TRR and bound EDA and/or GLY, ca.10%. Therefore, a minimum of 53% of the TRR in breast muscle was not characterized.

Table 25. Distribution of radioactivity in fractions of kidney from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 1.98 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
Aqueous	(21.1)	
Neutral	(5.0%; analyzed using TLC)	
EU	3.55	0.071
Origin/unknown	1.6	
Basic	(10.8%; analyzed using TLC)	
EDA/GLY	3.74	0.074
EU	0.238	0.005
EBIS	1.02	0.020
ETU/JB	0.183	0.004
Origin/unknown	5.6	
Acidic	4.7	
Chloroform (lipid)	3.7	
Water	1.4	
Unextracted	(73.0)	
Acid hydrolyzed	(70.0%; analyzed using TLC)	
EDA/GLY	25.76	0.510
ETU	0.77	0.015
EU	1.68	0.033
NAcEDA	6.02	0.119
HYD	6.9	0.137
EBIS	0.42	0.008
Origin/unknown	20.37	
Protease hydrolyzed	(67.5)	

Table 26. Distribution of radioactivity in fractions of liver from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 1.92 ppm).

Fraction/ metabolite	Percent of TRR	Mancozeb equivalents (ppm)
First extraction		
Methanol:water	(33.6%; analyzed using TLC)	
ETU	0.3	0.006
EU	4.5	0.086
NAcEDA	0.4	0.008
HYD/IMID	2.2	0.042
GLY/EDA	4.1	0.079
Origin/unknown	25.7	
Chloroform	4.1	
Water	8.8	
Chloroform:Methanol	1.0	
Unextracted	(49.2)	
Acid hydrolyzed	(44.9)	
Basic	41.2	
Neutral	0.6	
Acidic	0.8	
Protease digested	(42.5)	
Basic	(34.8% analyzed using TLC)	
EBIS	0.3	0.007
ETU/JB	0.4	0.008
EU	0.5	0.010
NAcEDA	0.6	0.011
HYD	1.5	0.030
IMID	2.5	0.049
EDA/GLY	9.8	1.89
Origin/unknown	17.4	
Neutral	0.3	
Acidic	0.5	
Second extraction		
Extracted (unspecified)	42.3	
Unextracted	57.7	
Protease digested	(51.5; dansylated and analyzed using TLC)	
Dansyl-EDA	3.2	0.062
Dansyl-NAcEDA	0.9	0.017

Table 27. Summary of residues in hen eggs and tissues.

Component	Percentage of TRR			
	Egg	Muscle	Kidney	Liver
Identified degradates	51.28	40.2	50.28	27.1
Unidentified	15.36	16.4	27.57	43.0
Unanalyzed extracted	7.7	23.1	9.8	14.7
Unhydrolyzed	5.5	7.4	3.0	6.7
Unexplained	22.8	12.1	9.35	8.5

The registrant additionally presented data concerning residues of mancozeb and ETU analyzed using GC methods; the reported residues were corrected for method recovery. For comparison, ETU residues estimated using TLC on silica gel plates developed with ethyl acetate:2-propanol:water (65:25:10, v:v:v) and 2-propanol:ammonium hydroxide (4:1, v:v) are presented below in Table 28. The metabolites were visualized and quantified using the previously described methods.

Table 28. Mancozeb (CS_2-containing residues) and ETU in excreta, eggs, and tissues from hens dosed at 36 ppm.

Sample	Mancozeb (ppm)	ETU (ppm)	ETU (ppm)
Excreta	23.1	3.71	ND[a]
Whole Egg	0.012	0.057	0.06
Breast	0.037	<0.007	ND
Thigh	0.069	<0.007	ND
Liver	0.165	0.003	0.004
Gizzard	0.15	0.007	ND
Kidney	0.14	<0.007	<0.007
Fat	0.13	0.01	ND

[a] ND indicates no detectable residue on the TLC.

After reexamining the poultry metabolism data, we conclude that the requirement for additional data remains outstanding. Only ca. 30-50% of the TRR in eggs and tissues was characterized, and most of those identifications are considered tentative due to poor separation of metabolites on TLC or the failure to perform confirmatory analyses. In eggs, the only metabolites with verified identities were ETU (up to 7% of the TRR) and glycine (maximum of 10%; uncertain due to the co-migration of EDA with underivatized glycine on TLC). In liver, the presence of ETU was confirmed (<1% of the TRR), as were NAcEDA (1%) and EDA (percentage undetermined due to co-migration of glycine with EDA). We do not consider unanalyzed fractions from ion exchange

chromatography or radioactivity at the origin of TLC plates to be sufficiently characterized. With regard to the lack of data on metabolites in fat, we maintain that these data requirements remain outstanding.

RESIDUE ANALYTICAL METHODS

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required multiresidue testing for mancozeb and ETU. The Mancozeb Residue Chemistry Chapter, dated 9/86, required the registrant to develop methodology specific for mancozeb and suitable for enforcement purposes.

In response to the Guidance Document, the Mancozeb Task Force submitted multiresidue test data (1988: MRID 40764601); these data have been forwarded by EPA to the Food and Drug Administration (FDA) for review. According to the Pestrak data base (10/13/89; PAM Vol. I, Appendix), mancozeb is not likely to be recovered by FDA Multiresidue Protocols A-E; special surveys have occurred with other methods. ETU is variably recovered by Protocol A using special gas chromatography (GC) or high performance liquid chromatography (HPLC) methods; special surveys have also been conducted on ETU with other methods.

The analytical methods currently in use today for mancozeb determination are all modifications of the basic dithiocarbamate method described by Pease (JAOAC 40:1113-1118). These methods are based on the liberation of carbon disulfide from the EBDC moiety by acid digestion in the presence of stannous chloride, followed by determination of the carbon disulfide produced using colorimetry or GC. These methods are not specific for the individual EBDCs analyzed and will not differentiate other degradates such as EBIS that may be converted to carbon disulfide. Plant residue data reviewed in this document were analyzed using the Keppel method (JAOAC, 54:528-532). This method is listed as method III in PAM Vol. II and currently is used by FDA for enforcement purposes. Mancozeb residues are decomposed to carbon disulfide by refluxing with boiling dilute acid. Evolved carbon disulfide is carried through a trap to remove hydrogen sulfide and other volatile interferences. In a second trap, the carbon disulfide is reacted to form a yellow complex, cupric salt of N, N-bis(2-hydroxyethyl)dithiocarbamic acid, which is measured colorimetrically at 435 nm. A standard curve is prepared by carrying several amounts of analytical standards of mancozeb through the method and is constructed using linear regression.

A description of GC methods for the determination of EBDCs in crops and processed products (MTF-89-AM-001, G. Westberg, Morse Laboratories, 6/7/89), meat (ETU-89-AM-002, G. Westberg, Morse Laboratories, 8/25/89), and milk (ETU-89-AM-003, G. Westberg, Morse Laboratories, 8/25/89) were submitted (MRID 41343101) and reviewed by the Agency (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) for the EBDC/ETU monitoring study. By these methods, EBDCs are decomposed by reaction with HCl/stannous chloride and EDTA to carbon disulfide. Evolved carbon disulfide is analyzed using GC using equipped with an Alltech 223 packed column and a flame photometric detector (FPD) in the sulfur mode.

Analytical methodology for ETU is based on the original method published by Onley and Yip (JAOAC 54:165-169). ETU is extracted with aqueous methanol, cleaned up by column chromatography and then analyzed by GC as the S-butyl derivative, following reaction of ETU with 1-bromobutane. Derivatized ETU may also be quantitated using GC with a sulfur specific detector; alternatively, underivatized ETU may be determined using HPLC with a reverse phase C-18 column (Morse Laboratories 7/27/89). Plant residue data reviewed in this document were analyzed using HPLC and gas liquid chromatography (GLC) method. By the GLC method, the crop is extracted with methanol, the methanol extract (containing ETU) is concentrated by rotary evaporation, and cleaned up on an alumina column. The concentrated extract is derivatized with 1-bromobutane to form butyl-ETU. The butyl-ETU is extracted with chloroform, solvent exchanged into toluene, and analyzed using GLC with a 10% carbowax column with flame photometric detection (sulfur mode). Quantitation is by external standard using ETU standards in toluene. A standard curve is prepared over the concentration range of interest, using peak height measurements.

Methodologies for ETU determination in crops (MTF-88AM-004, E. Rodgers, K. Tufts, G. Westberg, Morse Laboratories, 7/10/87, revised 7/27/89), meat (ETU-89AM-004, E. Rogers, K. Tufts, S. Normington, and G. Westberg, Morse Laboratories, draft 9/13/89), and milk (ETU-89AM-005, E. Rodgers, K. Tufts, S. Normington, and G. Westberg, Morse Laboratories, draft 9/13/89) were submitted (MRID 41343101) and reviewed by the Agency (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) for the EBDC/ETU monitoring study. These methods involve extraction of ETU using methanol or ethanol, filtration through celite, concentration, and clean-up on a alumina column. The concentrated extract is analyzed using HPLC with a reverse phase C-18 column, 5% methanol in water as the mobile phase, and UV or electrochemical detection.

At the present time, analytical methods converting all EBDCs and some metabolites to carbon disulfide will be considered adequate for enforcement, along with a specific method for ETU. If any

additional residues on concern are found in the metabolism studies currently in progress, additional methodology may be required. The following data requirement remains outstanding:

- If the requested data regarding the nature of the residue in plants and animals reveal additional metabolites of toxicological concern, additional analytical methods for data collection and enforcement may be required.

References (used):

MRID(s): 40764601. 41343101.

Discussion of the data:

The Mancozeb/ETU Task Force submitted a preliminary report (MRID 41343101) pertaining to the method validation which has been reviewed by the Agency (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) for the EBDC/ETU monitoring study. EBDC (mancozeb) and ETU residues in crops, processed commodities, milk, and meat were analyzed using Morse Laboratory methods. Descriptions of these methods, summarized by CBRS (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) are reiterated here for clarity.

EBDCs in crop and processed commodities (MTF-89-AM-001, G. Westberg, Morse Laboratories, 6/7/89), meat (ETU-89-AM-002, G. Westberg, Morse Laboratories, 8/25/89), and milk (ETU-89-AM-003, G. Westberg, Morse Laboratories, 8/25/89): EBDC residues in frozen, ground crop and processed commodity samples or meat samples or quick thawed milk samples are decomposed by reaction with HCl/stannous chloride in a sealed reaction flask in a boiling water bath. EDTA solution is added to the flask before reaction. Evolved carbon disulfide in the headspace (airspace) is analyzed using headspace GC with an Alltech 223 packed column and a flame photometric detector (FPD) in the sulfur mode after the column is preconditioned with CS_2. Standards and fortified samples are prepared and analyzed in the same manner. The limit of detection was reported to be 0.02 ppm. Quantitation is by external standard and a calibration curve on log/log paper.

ETU in crops (MTF-88AM-004, E. Rodgers, K. Tufts, G. Westberg, Morse Laboratories, 7/10/87, revised 7/27/89): ETU is extracted from the chopped crop or meat samples, or milk samples with water:ethanol (crops and milk) or water:methanol (meat), pH adjusted to 11-12 with NH_4OH. The extract is pH adjusted to 7-9, filtered through celite, concentrated by rotary evaporation with a decanol keeper, and cleaned up on a alumina column. The ETU is eluted with ethanol:chloroform (4:96 or 6:94, v:v). The eluate is concentrated by rotary evaporation. The concentrated extract is analyzed using HPLC with a reverse phase C-18 column, 5% methanol in water as the mobile phase, and detection by UV at 233

nm or by electrochemical detection. Quantitation is by external standard using a calibration curve. The limit of detection of the method was reported to be 0.01 ppm for crops and was not reported for meat or milk. Although not documented in the method, electrochemical detection was used for tomato paste.

The recoveries of mancozeb and ETU from fortified crop, milk, and meat samples are presented in Table 35.

Table 35. Recovery of mancozeb and ETU from fortified crop, milk, and meat samples.

Matrix	Laboratory	Fortification level (ppm)	Recovery (%)
Mancozeb:			
Apple	Craven[a]	0.02-2.0	96-102
Banana	Craven[a]	0.02-2.0	91-109
Celery	McKenzie	0.02-2.0	90-94
Snap beans	McKenzie	0.02-2.0	88-97
Corn	EN-CAS	0.02-2.0	Not complete
Potato	Morse	0.02-2.0	89-92
Tomato	Morse	0.005-0.02	98-115
Milk	Morse	0.002-0.02	108-110
Meat	Morse	0.002-0.02	82-103
ETU:			
Apple	Craven[a]	0.01-1.0	78-87
Banana	Craven[a]	0.01-1.0	88-106
Celery	McKenzie	0.01-1.0	82-100
Snap beans	McKenzie	0.01-1.0	79-87
Dry beans	EN-CAS	0.01-1.0	75-84
Corn	EN-CAS	0.01-1.0	81-91
Potato	Morse	0.002-1.0	79-102
Tomato	Morse	0.002-0.01	79-93
Tomato paste	Morse	0.002-0.01	76-84
Milk	Morse	0.001-0.01	72-88
Meat	Morse	0.001-0.01	67-74

[a] Data from Craven Laboratories are not used in this Update document to support the requirements for reregistration.

For purposes of the EBDC/ETU monitoring study, CBRS concluded the following: (i) analytical methods must be validated in each matrix (commodity) for which data are to be submitted; (ii) the recovery values reported for the matrices tested (apples, bananas, celery, snap beans, potatoes, tomatoes, milk, and meat) were adequate; however, recovery data are still needed for each commodity study submitted and recovery must be determined with each set of samples analyzed; (iii) chromatograms submitted for EBDC analyses indicate interferences in tomatoes, meat, and milk;

and (iv) the residue levels must be measured and reported at the lowest limit of detection possible.

STORAGE STABILITY DATA

Conclusions:

The Mancozeb Guidance Document, dated 4/87, concluded that the available storage stability data are adequate to demonstrate that mancozeb is stable in or on frozen apple and tomato samples for up to 12 months, and ETU is stable for up to 6 months. The Guidance Document required storage stability studies on both weathered and fortified frozen samples from representative crops from each crop grouping and fortified storage stability data for processing studies. In addition, the Guidance Document required storage stability data depicting the decline in residues of mancozeb and percentage decline or increase of ETU for animal commodities.

In response to the Guidance Document, the Mancozeb Task Force submitted storage stability data (MRID 41070001) for selected crops which were reviewed by CBRS (EPA Memorandum CBRS No. 5280, S. Hummel, dated 8/17/89). CBRS concluded that under the conditions used by the laboratory (Enviro-Bio-Tech Ltd.) performing the study, mancozeb is stable in or on apples, tomatoes, and wheat for six months. ETU is stable in tomatoes and wheat for six months, but only stable for one month in frozen apples. CBRS stated that storage stability data by Enviro-Bio-Tech Ltd.

In an Agency memorandum (EPA Memoranda CBRS Nos. 4656, 4707, and 4995, S. Hummel, dated 10/25/90), it was concluded that although no additional storage stability data are required to support the previously reviewed residue field trials, storage stability data are required for additional residue field trial studies submitted.

The ETU Task Force submitted storage stability data (MRID 41643601) with the fourth quarter and final report for the EBDC/ETU monitoring study as required by the EBDC Special Review Data-Call-In Notice of 3/10/89. These data were reviewed by S. Hummel (CB No. 7155, and HED No. 0-2032, dated 12/4/90) who concluded that under the storage conditions used in the market basket survey, these data indicate that mancozeb (fortified samples) was stable for only 1 month in potatoes, for up to 4 months in dry beans, frozen corn, lettuce, and for up to 6 months in tomatoes, meat, and milk. It was further concluded that ETU was stable for three months or longer in coarsely ground fortified samples of dry beans, corn, meat, milk, and tomatoes; 2 months in lettuce; and 0.5 months in potatoes. In finely ground fortified samples, ETU was stable for 12 days in dry beans,

frozen corn, lettuce, tomato, and meat; ETU was stable for only 5 days in potatoes. No weathered storage stability data are available on representative crops where mancozeb uses are allowed.

Rohm and Haas Company submitted data (1991; MRID 41976101; CBRS No. 8513) performed by Enviro-Bio-Tech Ltd. pertaining to the storage stability of mancozeb and ETU in or on whole apples that had been sprayed with mancozeb or ETU. These data indicate that residues of mancozeb are stable in or on fortified whole apples samples for up to 549 days of frozen storage. The data also indicate that residues of ETU are stable for up to 31 days in or on whole apples treated with ETU. Frozen storage stability of ETU residues in or on whole apples treated with mancozeb could not be determined because the ETU recovery percentages were quite variable. Recoveries of ETU from mancozeb-fortified samples ranged from 63% (day 184) to 180% (day 31); although recoveries of ETU greater than 100% indicate conversion of mancozeb to ETU, the calculated conversion factors were rather negligible (0.1-2%).

The samples from field residue and processing data reviewed in this Update document were analyzed by Enviro-Bio-Tech Ltd., with the exception of processed potato samples (MRID 41091601) which were analyzed by National Food Laboratory (Washington, D.C.). In these studies, mancozeb analyses were conducted using a colorimetric method (Keppel) and ETU analyses were conducted using a GLC method (Onley). A summary of the duration of frozen storage prior to analysis for each crop and processed products reviewed in this Update is presented in Table 36. The results of storage stability studies of mancozeb and ETU in various raw agricultural commodities under frozen conditions are presented in Tables 37 through 42.

The field residue data submitted for tomatoes, cranberries, field corn grain, and seed treatment of wheat grain are supported by acceptable storage stability data.

The field residue data submitted for potatoes, apples, sweet corn, and wheat grain (seed treatment) are not supported by storage stability data because samples were stored at intervals longer than when either mancozeb or ETU are stable under the same conditions.

No storage stability data are available for asparagus, bananas, cucumbers, field corn fodder, grapes, onions, papayas, peanuts (nutmeats, vines, hay, and hulls), pears, potatoes (processed products), sugar beets and sugar beet tops, sweet corn (cannery waste), wheat straw, and seed treatments (stems and leaves). No data have been submitted concerning the storage stability of mancozeb residues of concern in animal tissues. The following data requirements remain outstanding:

- To support the field residue and processing data required in this Update document, storage stability studies must be concurrently conducted (in the same laboratory, under the same conditions, and for the same duration) with the field residue and processing studies. If samples from the field residue and processing studies are analyzed within two weeks of collection, and all fresh samples are frozen within a few hours of collection, and all analyses are completed on the same day on which they were begun (from grinding the sample through the determinative step), then the requirement for concurrent storage stability data may be waived. Protocols for these studies must be submitted to and approved by the Agency prior to initiating the studies.

- If cattle and poultry feeding studies are required, then fortified storage stability studies will be required on all animal commodities (i.e. tissues, milk, and eggs) for which residue data are submitted to the Agency. Analyses must be conducted over a time period that includes the time interval that each commodity is held in frozen storage prior to residue analyses.

- The nature of the residue in plants and animals is not adequately understood. If the requested data on plant and animal metabolism indicate the presence of additional metabolites of toxicological concern, data depicting stability of these residues during storage will be required.

Table 36. Summary of the duration of storage (frozen) for commodities reviewed in this document.

MRID	Commodity	Days of Storage Mancozeb	Days of Storage ETU
41092007	apples	34-427	39-432
41976101	apples	0-549	0-549
40869701	asparagus	292	292
40869702	asparagus	459	494
40913303	bananas	196	199
40913304	bananas	168	63
40869705	field corn	109	44
41091701	processed field corn	208-215	209-210
41093201	sweet corn	41-343	49-347
40869706	cranberry	31	33
41092006	cucumbers	389-413	396-418
40869707	cucumbers	553	496
41092001	grapes	97-114	131-148
41092002	grapes	52-57	64
41483801	processed grapes	231	235-267
40869708	onions	336-350	346-360
41092003	onions	37	44
40869709	papaya	40	48
40869710	papaya	63	71
40869711	peanuts	17	17
41092004	peanuts	408	412
40913306	pears	108-122	383-397
40913301	potatoes	307-324	309-326
41091601	potatoes	13	15
41091601	processed potatoes	152-244	152-244
40869712	sugar beets	286-314	286-322
41091801	seed treatment	14-82	25-212
40768001	processed tomatoes	7-33	14-40
40869713	tomatoes	314-324	319-329
40869714	tomatoes	101-112	97-117
41092005	wheat	483	478
40869716	wheat	57-78	65-86
40869715	wheat	70	74

References (used):

MRID(s): 41070001. 41643601. 41976101.

Discussion of the data:

Rohm and Haas Company (1989; MRID 41070001, Report No. 34C-88-56) submitted data from a study performed by Enviro-Bio-Tech Ltd. pertaining to the storage stability of mancozeb and ETU in or on apples, tomatoes, and wheat. Commodities from untreated residue studies were analyzed for mancozeb and ETU to confirm the initial absence of these compounds. The untreated samples were then fortified with mancozeb at 1 ppm or with ETU at 0.1 ppm. The fortified samples were immediately (day 0) analyzed and stored at -20 C for 30, 180, 365, and 730 days. The commodities were analyzed for mancozeb using a colorimetric method (Pease as modified by Keppel; JAOAC, 54:528-532) and for ETU using an HPLC method (modified Onley method; JAOAC, 60:1105-1110). The limit of detection was 0.5 ppm for mancozeb and 0.02 ppm for ETU. The stability of mancozeb and ETU between 0 and 24 months is presented in Table 37; the method recovery for each commodity is presented in Table 38.

Table 37. Percentage recovery of residues from apples, tomatoes, and wheat fortified with mancozeb at 1 ppm and ETU at 0.1 ppm and stored frozen (-20 C) for 0-24 months.

	Percentage Recovery[a]									
	Mancozeb (months)					ETU (months)				
Commodity	0	1	6	12	24	0	1	6	12	24
Apples	100	103	101	75	76	95	103	64	46	50
Tomatoes	103	101	98	71	76	96	101	82	76	58
Wheat	98	100	102	81	76	92	102	87	72	60

[a] Reported values for mancozeb were corrected for average method recovery using 97% for apples, 97% for tomatoes, and 99% for wheat. Reported values for ETU were also corrected using 94% for apples, 95% for tomatoes, and 94% for wheat.

Table 38. Method recovery for mancozeb and ETU from apples, tomatoes, and wheat.

	Method Recovery (%)									
	Mancozeb (months)					ETU (months)				
Commodity	0	1	6	12	24	0	1	6	12	24
Apples	95	97	97	98	100	87	90	94	96	101
Tomatoes	95	97	97	97	98	83	94	98	100	102
Wheat	94	98	100	101	102	89	92	94	94	101

The data presented on previous tables indicate that mancozeb and ETU residues decline in apples, tomatoes, and wheat under the tested conditions. Decline of mancozeb in these commodities for the tested intervals appears to be limited. However, ETU residues declined rapidly in apples after 1 month of frozen storage and in tomatoes and wheat after 12 months of storage. Additional storage stability data are required to support field residue and processed products data submitted for tolerance assessment.

The ETU Task Force (MRID 41643601) submitted storage stability data with the fourth quarter and final report for the EBDC/ETU monitoring study as required by the EBDC Special Review Data-Call In-Notice of 3/10/89. An updated report (MRID 41831401) was submitted with additional storage intervals for dry beans and corn. These data were reviewed by the Agency (CB No. 7155, and HED No. 0-2032, S. Hummel, dated 12/4/90 and CB No. 7901, HED No. 1-1089, S. Hummel, dated 5/4/92) and are reproduced in Tables 39 and 40 for information purposes.

Table 39. Storage stability of mancozeb in finely ground frozen raw agricultural commodities from the EBDC/ETU Market Basket Survey.

	Percent of original amount at intervals (months)						
Commodity[a]	0	0.5	1	2	3	4	6
Beans, dry	84	123	102	117	108	98	120
Corn, frozen	85	113	101	96	90	86	103
Lettuce	97	96	91	91	87	95	NA
Potato	100	84	77	59	NA	NA	NA
Tomato	96	90	91	NA	92	NA	100
Meat	100	98	92	NA	112	NA	112
Milk	102	109	89	NA	98	NA	79

[a] Crop samples were fortified at 2 ppm; meat and milk samples were fortified at 0.5 ppm.

Table 40. Storage stability of coarsely ground and finely ground commodities fortified with ETU.

Commodity[a]	Coarsely ground (months)						Finely ground (days)		
	0	0.5	1	3	4	6	0	5	12
Beans, dry	91	96	97	81	85	94	79	95	95
Corn, frozen	83	97	102	95	95	89	85	103	101
Lettuce	113	94	107	55	NA	NA[b]	97	103	117
Potato	99	84	64	47	NA	NA	92	72	76
Tomato	100	104	105	93	NA	89	97	103	97
Meat	102	108	106	95	NA	110	101	112	108
Milk	94	97	106	95	NA	96	NA	NA	NA

[a] Crop samples were fortified at 0.5 ppm; meat and milk samples were fortified at 0.1 ppm.
[b] NA indicates not analyzed.

These data indicate that mancozeb (fortified samples) was stable for only 1 month in potatoes, for up to 4 months in dry beans, frozen corn, lettuce, and for up to 6 months in tomatoes, meat, and milk. The Agency concluded that ETU was stable for three months or longer in coarsely ground fortified samples of dry beans, corn, meat, milk, and tomatoes; 2 months in lettuce; and 0.5 months in potatoes. In finely ground fortified samples, ETU was stable 12 days in dry beans, frozen corn, lettuce, tomato, and meat; but ETU was stable for only 5 days in potatoes.

Rohm and Haas Company (1991; MRID 41976101; CBRS No. 8513) submitted data from a study performed by Enviro-Bio-Tech Ltd. pertaining to storage stability of mancozeb and ETU in or on apples. A group of 100 whole apples were sprayed with 1,000 ppm ai solution of mancozeb in acetone (80% WP formulation); this rate is equivalent to 1.2 lb ai/A. A second group of 100 whole apples were sprayed with a 100 ppm ai solution of ETU in water; this rate is equivalent to 0.12 lb ai/A. After spraying, the apples were allowed to air-dry for one hour, separated into subsamples of seven apples each, and stored in a freezer at -18 to -20 C. An identical number of untreated apples were stored frozen for each subsample. Samples were shipped frozen the same day as treatment and stored at -20 C (±5 C) upon receipt at the laboratory and were kept frozen until analyzed, except for day-0 samples which were analyzed the same day as received. Untreated apples were immediately analyzed to confirm the initial absence of mancozeb and ETU, and were fortified with mancozeb at 0.05-2 ppm or with ETU at 0.01-0.1 ppm. The stored apples were removed from storage one day prior to analysis, thawed for 10 minutes, homogenized with dry ice, and returned to frozen storage for 24 hours prior to analysis. Apples were removed from frozen storage

at intervals of 14, 30, 61, 121, 183, 365, and 548 days. The method recoveries of mancozeb and ETU from fortified, untreated apple homogenates were conducted at each analysis date. Mancozeb analyses were conducted using a colorimetric method (Pease, as modified by Keppel; JAOAC, 54:528-532); ETU analyses were conducted using a GC/FPD method (Onley; JAOAC, 60:1105-1110). The limit of detection was 0.05 ppm for mancozeb and 0.01 ppm for ETU. Data pertaining to the storage stability of residues of mancozeb and ETU are presented in Table 41; the method recoveries of mancozeb and ETU from fortified apple samples at each sampling date are presented in Table 42.

Table 41. Storage stability of mancozeb and ETU in or on whole apples fortified with mancozeb and ETU.

	Mancozeb-treated			ETU-treated	
Storage (days)[a]	Mancozeb ppm[b]	Rec. (%)[c]	ETU ppm[b]	ETU ppm[b]	Rec. (%)[c]
0	1.68		0.032	0.072	
15	1.64	97.6	0.046	0.048	67.0
31	1.68	100	0.057	0.062	86.6
62	1.72	102	0.034	0.038	53.1
122	1.90	113	0.035	0.032	44.7
184	1.68	100	0.020	0.010	14.0
366	1.70	101	0.038	<0.01(ND)	-
549	1.61	95.8	0.030	<0.01(ND)	-

[a] Includes one day of frozen storage after homogenization of sample in dry ice.
[b] The results, calculated by study reviewer from the raw data, represent an average of duplicate aliquots from one subsample and were not corrected for method recoveries.
[c] Percent recoveries calculated by study reviewer from the raw data using the day-0 samples as 100% recovery. Conversion factor (percent) in parentheses.

Table 42. Method recoveries from stored, frozen, untreated apples fortified with mancozeb or ETU and analyzed concurrently with the storage stability samples.

Storage (days)[a]	Mancozeb Fort. (ppm)	Mancozeb Recovery (%)	ETU Fort. (ppm)	ETU Recovery (%)
0	0.05	84	0.01	89,116
	2	92	0.1	89,109
15	2	91,93	0.05	82,88
31	2	94,95	0.05	76,86
62	2	95,95	0.05	92,104
122	2	94,96	0.05	96,104
184	2	98,98	0.05	92,96
366	2	97,99	0.05	78
549	2	97,100	0.05	82,82

[a] Includes one day of frozen storage after homogenization of sample in dry ice.

The data presented in previous tables indicate that residues of mancozeb (fortified samples) were stable in or on whole apples treated with mancozeb for up to 549 days. Frozen storage stability of ETU residues in or on whole apples treated with mancozeb could not be determined because percent recoveries (based on day-0 residue data) were quite variable. Recoveries of ETU from mancozeb-fortified samples ranged from 63% (day 184) to 180% (day 31). Residues of ETU were stable for up to 31 days in or on whole apples treated with ETU.

MAGNITUDE OF THE RESIDUE IN PLANTS

The Mancozeb Guidance Document, dated 4/87, required additional crop field trials depicting residues of mancozeb, ETU and other residues of concern in or on apples, asparagus, bananas, carrots, celery, corn, cottonseed, cranberries, cucumbers, fennel, grapes, melons, onions, papayas, peanuts, pears, potatoes, sugar beet (roots and tops), summer squash, tobacco, tomatoes, and wheat. Additional data are also required for processed products of corn, cottonseed, grapes, peanuts, potatoes, and sugar beets. The Guidance Document also required residue data and proposal of tolerances to support registered seed or planting/propagation stock uses on caprifigs, flax, pineapples, rice, safflower, and sorghum.

According to the EBDC PD 4, only certain food/feed uses of mancozeb will be allowed, provided label revisions and residue data requirements are submitted. The food/feed uses of mancozeb allowed by the EBDC PD 4 are listed in Table 43. As a result of

the EBDC PD 4 ruling, the use of mancozeb on carrots and celery will no longer be allowed.

In response to the Guidance Document requirements, the Mancozeb Task Force submitted data for apples, asparagus, bananas, carrots, corn, cucumbers, cranberries, grapes, onions, papayas, peanuts, pears, potatoes, sugar beets, tomatoes, wheat, and crops with seed treatments. These submissions are detailed by topic in the "INTRODUCTION" section of this Update document.

The Mancozeb Task Force, has offered some of the listed data submissions, in whole or in part, to support a petition (1989; PP#9F3816) for the reduction of tolerances for residues of mancozeb in or on wheat grain (from 5 ppm to 1 ppm), wheat bran (from 20 ppm to 1 ppm), grapes (from 7 ppm to 3 ppm), peanuts (from 0.5 ppm to 0.1 ppm), and sugar beets (from 2 ppm to 1 ppm) and the establishment of a permanent tolerance for potatoes (from the interim tolerance of 0.5 ppm to 0.1 ppm). The Agency has reviewed this petition in a memorandum by S. Hummel (CBRS No. 5964 dated 10/12/90) who concluded that the evaluation of these proposed tolerance revisions will require resubmission of the petition to include Sections A, B, and C.

The Mancozeb Task Force members separately submitted applications/proposals to amend their product labels to incorporate maximum number of applications and restore mancozeb uses on other crops. These applications were reviewed by S. Hummel (CB Nos. 8439, 8413, 9110, and 9115 dated 1/22/92; CB Nos. 8536-8 and 8441-3 dated 1/28/92; and CB Nos. 8571, 8410, 8411, 8992, 8993, 8995, 9097, 9098, and 9001 dated 1/28/92. These applications are now superseded by the EBDC PD 4.

Since issuance of the Guidance Document, the intrastate registrations for the 5.6% D formulation (EPA Reg. No. 31143-4466) in TX and the 4.8% D formulation (EPA Reg. No. 6023-3043) in CA have been canceled. Rohm and Haas has stated that they have no mancozeb registrations for D formulation and therefore, they do not intend to submit data reflecting this formulation class (EPA Memorandum CBRS No. 4015, S. Hummel, dated 9/27/88). CBRS concluded that no data reflecting the D formulation will be required, provided <u>all</u> dust uses are canceled. The Mancozeb Guidance Document data requirements for crop field trials using D formulations remain outstanding for food/feed use sites for which dust formulations are still registered (potatoes, tomatoes, and cucumbers). Registrants, other than members of the Task Force or other interested parties, who wish to retain the use patterns reflecting D formulation should be informed that additional data are required.

Table 43. Mancozeb uses allowed by the EBDC PD 4.

Crop	Rate (lb ai/A)	Maximum No. Applns.	Minimum Appln. Int. (days)	Minimum PHI (days)
Apples[a]				
-prebloom	4.8	4	7	bloom
-extended	2.4	7	7	77
Asparagus	1.6	4	10	180 120 CA/AZ
Bananas	2.4	10	14	0
Barley	1.6	3	7	26
Corn, field	1.2	10	--	40
Corn, sweet and pop				
-East of MS River, AR and LA	1.2	15	4	7
-West of MS River, except AR and LA	1.2	5	4	7
Cotton	1.6	4	--	May not be applied after bolls open
Crabapples/Quince[a]				
-prebloom	4.8	4	7	bloom
-extended	2.4	7	7	77
Cranberries	4.8	3	7	30
Cucumbers	2.4	8	7	5
Fennel	1.6	8	7	14
Grapes				
-East of Rocky Mtns.	3.2	6	7	66
-West of Rocky Mtns., except CA	2	3	7	66
-CA	2	3	7	bloom
Melons	2.4	8	7	5
Oats	1.6	3	7	20
Onions, dry bulb[b]	2.4	10	7	7
Papayas	2	14	14	0
Peanuts	1.6	8	7	14
Pears[a]				
-prebloom	4.8	4	7	bloom
-extended	2.4	7	7	77
Potatoes	1.6	7	5	14 3 in CT, FL, MA, ME, NH, NY, PA, VT, and WI
Rye	1.6	3	7	26
Squash, summer	2.4	8	7	5
Sugar beets	1.6	7	7	14
Tomatoes				
-West of MS	1.6	4	7	5
-East of MS	2.4	7	7	5
Wheat	1.6	3	7	26

[a] Treatment schedules may not be combined or integrated.
[b] Application to exposed bulbs is prohibited.

Rohm and Haas submitted a summary (MRID 40258301) of previously submitted data comparing ground and aerial applications. Currently, the Agency no longer requires crop field trials reflecting aerial application in cases where adequate data are available from the use of ground equipment reflecting the same application rate, number of applications, and preharvest intervals, provided that the product label specifies aerial applications are to be made in a minimum of 2 gal/A of (or 10 gal/A in the case of tree crops). See CB memorandum dated 12/6/91 by R. Quick (Requirements for Crop Field Trials to Support Aerial Applications).

The Guidance Document required storage stability data to reflect the storage intervals of all raw and processed commodity samples analyzed for mancozeb, ETU, and other residues of concern. The Agency (EPA Memorandum CBRS No. 7134, S. Hummel, dated 11/26/90) noted differences and variability in the stability of ETU in frozen storage which were attributed to many factors including the specific commodity, storage conditions, and sample handling. As a result, the Agency requires that storage stability studies must be concurrently conducted with the residue field trial studies. The availability of these storage stability data are noted in each crop section.

The use patterns discussed in the following sections include only those end-use products registered to the Mancozeb Task Force [Rohm and Haas, Ciba-Geigy, E. I. du Pont, and Atochem (formerly Pennwalt)]. The registered uses are based on the product labels of the above listed registrants according to the EPA Site Listing (SP05) dated 9/25/90. A list of mancozeb end-use products along with the formulation classes registered to the Task Force is presented in Table 44.

Table 44Mancozeb end-use products registered to Atochem (formerly Pennwalt), Ciba-Geigy, E.I. du Pont, and Rohm and Haas.

Registrant	Formulation	EPA Reg. No.	Accepted Date
Ciba-Geigy	48% WP	100-629	01/09/90
Ciba-Geigy	70% WP	100-689	12/01/88
E.I. du Pont	37% FlC	352-398	12/28/89
E.I. du Pont	80% FlC	352-341	12/28/89
E.I. du Pont	75% DF	352-449	12/28/89
Atochem	62% WP	4581-358	03/26/90
Atochem	75% DF	4581-370	04/26/90
Rohm & Haas	70% DF	707-179	12/28/89
Rohm & Haas	75% DF	707-180	02/08/88
Rohm & Haas	32% FlC	707-162	01/17/83
Rohm & Haas	37% FlC	707-156	02/08/88
Rohm & Haas	80% WP	707-78	02/08/88
Rohm & Haas	80% WP	707-97	01/04/83

The use patterns and residue data discussed in this Update are based on the current labels and data submissions made by the Mancozeb Task Force. When end-use products DCIs are developed (e.g. at the issuance of RED), RD should require that all end-use product labels (e.g. any unamended basic producer labels, SLNs, and products covered under generic data exemption) be amended such that they are consistent with basic producer labels.

Root and Tuber Vegetables Group

Carrots

Conclusions:

The EBDC PD 4 does not allow continued use on carrots. All carrot uses must be deleted from product labels. The following are required:

- Revised labels deleting carrots from all registered mancozeb products. No additional data are required for carrots, provided use directions for carrots are deleted from all mancozeb labels. If, however, any use on carrots is continued for any reason, then full supporting residue data will be required for the label use pattern.

References (not used):

[The following reference(s) pertain to uses of mancozeb which are no longer allowed by the EBDC PD 4.]

MRID(s): 40869703.

Discussion of the data:

N/A.

Potatoes

Tolerance(s):

An interim tolerance of 1 ppm has been established for the coordination product of zinc ion and maneb (calculated as zinc ethylenebisdithiocarbamate) in or on potatoes [40 CFR §180.319].

Use directions and limitations:

The 32 and 37% FlC, 37-80% WP, 70 and 75% DF formulations are registered for multiple foliar applications to potatoes at 0.6-1.6 lb ai/A on a 7- to 10-day interval using either ground or aerial equipment. These formulations are also registered for seed piece treatment at 0.78-1 lb ai/50 gal water. The 48 and 70% WP formulation (Ciba-Geigy EPA Reg. Nos. 100-629 and 100-689, respectively) specify a 7-day PHI. A maximum of four applications/season (totalling 4 lb ai/A), and a maximum seasonal use rate of 22.4 lb ai/A are specified for the respective 48 and 70% WP formulations. Except for the 48 and 70% WP formulations, no PHI, maximum number of applications, or maximum seasonal use rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for potatoes must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 5 days, and a minimum PHI of 14 days. A PHI of 3 days is allowed in CT, FL, MA, ME, NH, NY, PA, VT, and WI. Labels must state that use is recommended within an IPM program, and that vine kill should occur 14 days before harvest.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on potatoes harvested following multiple foliar applications of the WP and D formulations. In addition, the Guidance Document required revision of labels to specify the maximum seasonal rate or the maximum number of applications/season and establish a PHI. Processing studies were also required.

The earlier potato residue data discussed in the Residue Chemistry Chapter were inadequate because the treatments did not

reflect the maximum use pattern and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Potato samples were stored 4 to 85 days before analysis for mancozeb and 9 to 144 days before analysis for ETU. Samples from only one site (OH) were analyzed for ETU within 2 weeks of harvest (the time ETU remains stable in potatoes).

In response to the Guidance Document, the Mancozeb Task Force submitted field residue data (MRIDs 40913301 and 41091601) from tests conducted in CA and ID. Residue data from CA cannot be used to fulfill the requirements for reregistration since the potato samples from this test location were stored frozen for 307-324 days prior to analysis for mancozeb and for 309-326 days prior to analysis for ETU. The available storage stability data indicate that residues of mancozeb are only stable for up to one month and ETU residues are only stable for up to two weeks in or on potatoes.

Residue data from ID may be used to support the requirements for reregistration; the tests are supported by storage stability data and were conducted according to the use patterns allowed by PD 4. Residues of mancozeb were <0.05(nondetectable)-0.20 ppm, (which are below the interim tolerance of 1 ppm) in or on potatoes harvested 1 day following the last of five or six foliar applications at 1-15x the maximum single application rate or 0.9-11x the maximum seasonal application rate allowed by PD 4. Residues of ETU were <0.01 ppm (nondetectable) in or on these same samples. The submitted field residue data, however, do not fulfill the requirements for reregistration because geographical representation of adequate data is lacking. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum or 7 applications or 11.2 lb ai/A/season, a minimum application interval of 5 days, and a minimum PHI of 14 days. A PHI of 3 days is allowed in CT, FL, MA, ME, NH, NY, PA, VT, and WI. Additionally, labels must state that use is recommended within an IPM program, and that vine kill should occur 14 days before harvest.

- Data depicting mancozeb, ETU, and other residues of concern in or on potatoes harvested 3 days following the last of 7 applications at 1.6 lb ai/A/application at 5-day intervals. Tests must be conducted in CO(6%), ME(6%), OR(6%), WA(18%), and WI(6%); these states along with ID(28%) where data are available accounted for ca. 70% of the 1988 U.S. potato production (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

Samples must be frozen immediately after harvest and analyzed within two weeks of harvest.

The Mancozeb Task Force also submitted a processing study (MRID 41091601) depicting residues of mancozeb and ETU in the processed commodities of potatoes following treatment at 2 and 9x the maximum seasonal application rate allowed by PD 4. The available processing data indicate that residues of mancozeb concentrate in chips and dehydrated flakes, and that mancozeb residues are converted to ETU in dehydrated flakes, peels, and granules. Concentration factors could not be calculated, since residues were nondetectable in potatoes prior to processing. The processing data do not satisfy data requirements because (i) no data were submitted depicting residues in or on dry peels; (ii) no method recovery data were submitted for mancozeb residues in or on whole raw potatoes and in granules, or for ETU in granules; and (iii) no storage stability data were submitted from the performing laboratory, the National Food Laboratory; the limit of detection used in the processing study was four times higher than the limit of detection previously reported. The following data remain outstanding:

- Data depicting the potential for concentration of mancozeb, ETU, and other residues of concern in chips, granules, and wet and dry peel from potatoes bearing measurable weathered residues. If residues concentrate/convert in processed products, then appropriate food/feed additive tolerance must be proposed.

References (used):

MRID(s): 40913301. 41091601.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40913301 and 41091601) submitted data from four tests conducted in CA(1) and ID(3) pertaining to residues of mancozeb and ETU in or on potatoes following five or six foliar applications of the 80% WP formulation at 1.6, 8, and 24 lb ai/A/application (1, 5, and 15x the maximum single application rate allowed by PD 4) using ground (ID) and aerial (CA) equipment. The results are presented below.

State	No. of Applns. (G/A)	Rate (lb ai/A)	PTI (days)	Residues (ppm)[a] Mancozeb	ETU	Maximum Storage (days)
CA	1+4 (A)	1.6+2.4 = 11.2	0	<0.05	<0.01	326
CA	1+4 (A)	1.6+2.4 = 11.2	0	<0.05	<0.01	326
CA	1+4 (A)	1.6+2.4 = 11.2	5	<0.05	0.01	326
CA	1+4 (A)	1.6+2.4 = 11.2	5	<0.05	0.02	326
CA	1+4 (A)	1.6+2.4 = 11.2	15	<0.05	0.03	326
CA	1+4 (A)	1.6+2.4 = 11.2	15	<0.05	0.02	326
ID	6 (G)	1.6 = 9.6	1	<0.05	<0.01	15
ID	6 (G)	8.0 = 48.0	1	0.20	<0.01	15
ID	5 (G)	24.0 = 120.0	1	<0.05	<0.01	15

[a] Three samples each from CA and ID; reported values reflect duplicate analyses on each of three samples from CA.

Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on two untreated samples. Recoveries were 93% from one sample (ID test) fortified with mancozeb at 0.1 ppm, and 83 and 111% from two samples fortified with ETU at 0.05 and 0.01 ppm; reported residues were corrected for these recovery values. Recoveries were 87% from one sample (CA test) fortified with mancozeb at 0.05 ppm, and 93% from one sample fortified with ETU at 0.01 ppm; reported residues were corrected for these recovery values. Samples from ID were stored frozen (-20 C) for 13-15 days prior to analysis by Enviro-Bio-Tech, Ltd. Samples from CA were stored frozen (-10 C) for 307-324 days prior to analysis for mancozeb and for 309-326 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. Storage stability data pertaining to these storage intervals and conditions are available; see "STORAGE STABILITY DATA" section. These data indicate that residues of mancozeb are only stable for up to one month and ETU residues are only stable for up to two weeks in or on potatoes. Based on this information, only data from ID are supported by storage stability data since the potato samples from this test location were stored frozen for only 13-15 days prior to analysis.

The Mancozeb Task Force (1990; MRID 41091601) submitted data from a single study conducted in OH pertaining to residues of mancozeb and ETU in the processed products of potatoes. Potato tubers were harvested one day following the last of 13 foliar applications (using aerial equipment) of the 80% WP formulation

at 1.6 or 8 lb ai/A/application (1 or 5x the maximum single application rate, or 2 or 9x the maximum seasonal application rate allowed by PD 4). Residues of mancozeb and ETU were nondetectable (<0.2 and <0.02 ppm, respectively) in or on four samples of tubers treated at 1x and 5x. The raw unwashed potatoes were washed and processed according to simulated commercial procedures into peeled tubers (using abrasion or hand methods), peels (wet), chips, granules, and dehydrated flakes. The results are presented below.

Item	Residues (ppm)			
	Mancozeb	ETU	Mancozeb	ETU
	1x		5x	
Potatoes	<0.2	<0.02	<0.2	<0.02
Dehy. flakes	0.58-0.67[a]	0.03-0.17[b]	<0.2	0.1-0.39[c]
Chips	<0.2	<0.02	0.26-0.3[d]	<0.02
Peeled potatoes	<0.2	<0.02	<0.2	0.02-0.03[e]
Wet peels	<0.2	<0.02	<0.2	0.02-0.03[e]
Granules	<0.2	<0.02	<0.2	0.07-0.09[f]

[a] Concentration factor ≥2.9-3.4x.
[b] Conversion factor ≥5-75%; calculated as follows:
[(ETU product - ETU RAC)/Mancozeb RAC] x 100 = % Conversion.
[c] Conversion factor ≥40-185%.
[d] Concentration factor ≥1.3-1.5x.
[e] Conversion factor ≥0-5%.
[f] Conversion factor ≥25-35%.

Apparent residues of mancozeb and ETU were nondetectable (<0.2 and <0.02 ppm, respectively) in or on one untreated tuber sample and in one sample each of the processed products. Mancozeb analyses were conducted using a modified colorimetric method (Keppel) with a limit of detection of 0.2 ppm; ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.02 ppm. Recoveries were 92% from one sample of washed and peeled tubers, 63-79% from three samples of wet peels, and 58 and 79% from two samples of dehydrated flakes fortified with mancozeb at 0.24-0.56 ppm. Recoveries were 53 and 83% from two samples of unwashed whole tubers and 79 and 91% from two samples of peels fortified with ETU at 0.02 and 0.1 ppm. Samples were stored frozen for 152-244 days prior to analysis for mancozeb and ETU by the National Food Laboratory in Washington, DC. No concurrently conducted storage stability data were submitted to support this study.

Geographic representation of adequate data is lacking since the test state of ID only accounted for (28%) of the 1988 U.S. potato production (Agricultural Statistics Board, NASS, USDA Crop

Database, Aug. 1989). Residue data from a single test conducted in CA cannot be used to fulfill the requirements for reregistration since the potato samples from this test location were stored frozen for 307-324 days prior to analysis for mancozeb and for 309-326 days prior to analysis for ETU. The available storage stability data indicate that residues of mancozeb are only stable for up to one month and ETU residues are only stable for up to two weeks in or on potatoes.

Residue data collected from tests conducted in ID may be used to support the requirements for reregistration; the tests are supported by storage stability data and were conducted according to the use patterns allowed by PD 4. Residues of mancozeb were <0.05(nondetectable)-0.20 ppm, (which are below the interim tolerance of 1 ppm) in or on potatoes harvested 1 day following the last of five or six foliar applications at 1-15x the maximum single application rate or 0.9-11x the maximum seasonal application rate allowed by PD 4. Residues of ETU were <0.01 ppm (nondetectable) in or on these same samples. The submitted field residue data, however, do not fulfill the requirements for reregistration because geographical representation of adequate data is lacking. Additional field residue data from other potato-growing regions are required.

The available processing data indicate that residues of mancozeb concentrate in chips and dehydrated flakes, and that mancozeb residues are converted to ETU in dehydrated flakes, peels, and granules. Concentration factors could not be calculated, since residues were nondetectable in potatoes prior to processing. The processing data do not satisfy data requirements because no data were submitted depicting residues in or on dry peels and no method recovery data were submitted for mancozeb in whole raw potatoes and granules or for ETU in granules. In addition, no storage stability data were submitted from the performing laboratory, the National Food Laboratory; the method limit of detection used in the processing study was four times higher than the limit of detection previously reported. Additional processing data are required.

Sugar beets

Tolerance(s):

A tolerance of 2 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on sugar beet roots [40 CFR §180.176].

Use directions and limitations:

The 32, 37, and 80% FlC and 62 and 80% WP formulations are registered for multiple foliar applications to sugar beets at 1.2-1.6 lb ai/A/application. The 70% and 75% DF formulations are registered for the same use at 1.1-2.4 lb ai/A/application. Applications may be made using ground and aerial equipment and repeated at 7- to 10-day intervals. A 14-day PHI has been established. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for sugar beets must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on sugar beets harvested following applications of WP and D formulations using ground and aerial equipment in separate tests. In addition, the Guidance Document required revised labels specifying the maximum seasonal rate or the maximum number of applications/season. The Guidance Document also required processing data reflecting residues of concern in sugar beet pulp. According to the EPA Site Listing (SP05) dated 9/25/90, all D formulation uses on sugar beets have been canceled.

The earlier sugar beet residue data discussed in the Residue Chemistry Chapter were inadequate because the treatments did not reflect the maximum use pattern of multiple applications at 1.7 lb ai/A and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Sugar beet samples from 1985 field trials were stored 77 to 109 days before analysis for mancozeb and 65 to 197 days before analysis for ETU.

In response to the Guidance Document, Mancozeb Task Force submitted field residue data (MRID 40869712). These data indicate that residues of mancozeb did not exceed the established 2 ppm tolerance when harvested 1 or 15 days following treatments at 0.6x the maximum seasonal application rate allowed by PD 4. Residues of ETU were nondetectable (<0.01 ppm) in or on six samples from these same tests. The available data do not fulfill the requirements for reregistration because tests were not

conducted according to the maximum use pattern allowed by PD 4, geographical representation is inadequate, and no processing data were submitted. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

References (used):

MRID(s): 40869712.

Discussion of the data:

The Mancozeb Task Force (1988; MRID 40869712) submitted data from a single test conducted in ID pertaining to residues of mancozeb and ETU in or on sugar beet roots harvested 15 and 29 days following the last of four foliar applications (using ground equipment) of the 80% WP formulation at 1.6 lb ai/A/application (1x the maximum single application rate, 0.6x the maximum seasonal application rate allowed by PD 4). Residues of mancozeb were 0.057 and 0.076 ppm in or on two samples harvested 1 day posttreatment, and <0.05 ppm (nondetectable) in or on four samples. Residues of ETU were <0.01 ppm (nondetectable) in or on six samples. Reported residue values were corrected for method recovery using 82% for mancozeb and 93% for ETU. Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on one untreated sample. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 68% from one sample fortified with mancozeb at 0.05 ppm, and 97% from one sample fortified with ETU at 0.01 ppm. Samples were stored frozen (-10 C) for 286-314 days prior to analysis for mancozeb and for 286-322 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. Based on storage stability data for mancozeb and ETU on potatoes, residues would be expected to be stable in sugar beets stored frozen for 2 weeks.

Considering the newly submitted field trial data along with data reviewed in the Residue Chemistry Chapter, geographic representation is adequate since the test states of CA, TX, ID, and MN, along with neighboring states accounted for about 80% of the 1988 U.S. sugar beet production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data fulfill the requirements for reregistration because tests were conducted at the maximum use pattern allowed by PD 4, geographical representation is adequate. No processing data were submitted, however, a processing study was reviewed in the Residue Chemistry Chapter. Two samples were processed. Residues of mancozeb and

ETU did not concentrate in sugar beet molasses or white sugar. One sample of sugar beet pulp had residues of mancozeb 3x higher than in the rac. A feed additive tolerance is required. No additional data are required.

Leaves of Root and Tuber Vegetables Group

Sugar beet tops

Tolerance(s):

A tolerance of 65 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on sugar beet tops [40 CFR §180.176].

Use directions and limitations:

The 32, 37, and 80% FlC and 62 and 80% WP formulations are registered for multiple foliar applications to sugar beets at 1.2-1.6 lb ai/A/application. The 70% and 75% DF formulations are registered for the same use at 1.1-2.4 lb ai/A/application. Applications may be made using ground and aerial equipment and repeated at 7- to 10-day intervals. A 14-day PHI has been established. No maximum number of applications per season or maximum seasonal application rate has been established. Treated tops may not be fed to livestock. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for sugar beets must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on sugar beet tops harvested following multiple foliar applications (using ground and aerial equipment in separate tests) of the WP or FlC, and D formulations. In addition, the Guidance Document required revised labels specifying the maximum seasonal rate or the maximum number of applications/season. According to the EPA Site Listing (SPO5) dated 9/25/90, all D formulation uses on sugar beets have been canceled.

The earlier residue data on sugar beet tops discussed in the Residue Chemistry Chapter were inadequate because dust formulations were not represented and aerial field trials did not reflect the 14 day PHI. The dust formulation is not longer registered by Mancozeb Task Force members, and aerial field trial data are no longer needed, provided application is made in a minimum of 2 gal/A spray volume.

In response to the Guidance Document, the Mancozeb Task Force submitted field residue data (MRID 40869712). The submitted data indicate that residues of mancozeb exceeded the established tolerance (up to 99.5 ppm) in or on sugar beet tops harvested 15 days following treatment at 0.6x the maximum seasonal application rate allowed by PD 4. The registrant may have to propose a higher tolerance when all the required data have been submitted. Residues of ETU were 4.2-7.99 ppm in or on samples harvested 1 day posttreatment and were <0.01(nondetectable)-2.55 ppm in or on samples harvested 15 and 29 days posttreatment. No concurrently conducted storage stability data were submitted to support this study. However, a storage stability study was done for lettuce in connection with the EBDC/ETU Market Basket Survey. Residues of ETU were only stable for 2 months in frozen storage. The available data do not fulfill the requirements for reregistration because test was not conducted according to the maximum use pattern allowed by PD 4, and geographical representation is inadequate, even when the data discussed in the Residue Chemistry Chapter are considered. Earlier data which included ETU analyses were available only from TX and MN and only one MN field trial was similar to the PD 4 use pattern.

Further, we note that current labels for mancozeb use on sugar beets prohibit the feeding of treated tops to livestock. The Agency considers the restriction for sugar beet top grazing and feeding to be economically impractical (see memorandum by C. Trichilo dated 5/30/87: Economic Importance of Sugar Beet Grazing in Imperial Valley of CA). However, the Agency will consider retaining the feeding restriction on mancozeb labels. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

- Data depicting mancozeb, ETU, and other residues of concern in or on sugar beet tops harvested 14 days following the last of 7 foliar applications of a representative WP formulation at a maximum application rate of 1.6 lb ai/A applied at 7-day intervals. Tests must be conducted in CA(21%), ID(16%), and MI(10%), since these states accounted for ca. 70% of the 1988 U.S. sugar beet production (Ag. Statistics Board, NASS, USDA, Aug.

1989). Alternatively, the feeding restriction may be retained/reinstated on all mancozeb labels.

References (used):

MRID(s): 40869712.

Discussion of the data:

The Mancozeb Task Force (1988; MRID 40869712) submitted data from a test conducted in ID pertaining to residues of mancozeb and ETU in or on sugar beet tops harvested 1, 15, or 29 days following the last of four foliar applications (using ground equipment) of the 80% WP formulation at 1.6 lb ai/A/application (1x the maximum single application rate, 0.6x the maximum seasonal application rate allowed by PD 4). The results are presented on the following table.

State	No. of Applns.	Rate (lb ai/A)	PTI (days)	Residues (ppm)[a] Mancozeb	ETU	Maximum Storage (days)
ID	4	1.6 = 6.4	1	281	4.2	322
ID	4	1.6 = 6.4	1	289	7.99	322
ID	4	1.6 = 6.4	15	95	<0.01	322
ID	4	1.6 = 6.4	15	99.5	1.26	322
ID	4	1.6 = 6.4	29	51.8	1.03	322
ID	4	1.6 = 6.4	29	56.3	2.55	322

[a] Reported values reflect duplicate analyses on each of three samples.

Reported values were corrected for method recovery using 82% for mancozeb and 93% for ETU residues. Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively), in or on one untreated sample. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 95% from one sample fortified with mancozeb at 90 ppm, and 72-103% from three samples fortified with ETU at 0.04-5 ppm. Samples were stored frozen (-10 C) for 286-314 days prior to analysis for mancozeb, and for 286-322 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability data were submitted to support this study.

Geographic representation is inadequate since the test state of ID accounted for only 16% of the 1988 U.S. sugar beet production (Ag. Statistics Board, NASS, USDA, Aug. 1989), and including previously submitted data from MN, only 35% of sugar beet growing

areas are represented. The submitted data indicate that residues of mancozeb exceeded the established tolerance (up to 99.5 ppm) in or on sugar beet tops harvested 15 days following treatment at 0.6x the maximum seasonal application rate allowed by PD 4. Residues of ETU were 4.2-7.99 ppm in or on samples harvested 1 day posttreatment and were <0.01(nondetectable)-2.55 ppm in or on samples harvested 15 and 29 days posttreatment. No concurrently conducted storage stability data were submitted to support this study. Storage stability studies conducted on lettuce to support the EBDC/ETU Market Basket Survey showed ETU to be stable only 2 months in frozen storage. The available data do not fulfill the requirements for reregistration because test was not conducted according to the maximum use pattern allowed by PD 4, and geographical representation is inadequate. Additional data are required.

Bulb Vegetables Group

Onions

Tolerance(s):

A tolerance of 0.5 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on dry bulb onions [40 CFR §180.176].

Use directions and limitations:

The 48, 62, 70, and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered multiple foliar and in-furrow drench applications at planting to dry bulb onions at 1-2.4 lb ai/A/application using ground or aerial equipment. Applications may be repeated at 7-14 day intervals. A 7-day PHI is in effect. Foliar treatments are limited to four applications/season totalling 4 lb ai/A/season for the 48% WP formulation (EPA Reg. No. 100-629) and 12.6 lb ai/A/season for the 70% WP formulation (EPA Reg. No. 100-689); no limits on the number of applications/season or maximum seasonal rates have been established for other formulations. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for dry bulb onions must be revised to specify a maximum application rate of 2.4 lb ai/A/application, a maximum of 10 applications or 24 lb ai/A/season, a minimum application interval of 7 days, and

a minimum PHI of 7 days. Application to exposed bulbs will be prohibited.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data depicting residues in or on dry bulb onions harvested following applications of the WP and D formulations using ground and aerial equipment in separate tests. In addition, the Guidance Document required revised labels specifying the maximum seasonal rate or the maximum number of applications/season. According to the EPA Site Listing (SPO5) dated 9/25/90, all D formulation uses on dry bulb onions have been canceled.

The earlier onion residue data discussed in the Residue Chemistry Chapter were considered inadequate because PHI in most tests was too long and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage for 1985 field trials. Onion samples from 1985 field trials were stored 85 to 193 days before analysis for mancozeb and 97 to 218 days before analysis for ETU. Based on the potato storage stability data, residues were be expected to be stable in frozen storage for only 2 weeks.

In response to the Guidance Document, Mancozeb Task Force submitted field residue data (MRIDs 41092003 and 40869708). These data indicate that residues of mancozeb in or on two samples of dry bulb onions were below the established 0.5 ppm tolerance when harvested 7 days (the established PHI) following the last of 10 foliar applications of the 80% WP formulation at 2.4 lb ai/A/application (1x the maximum single and seasonal application rates allowed by PD 4). No concurrently conducted storage stability data were submitted to support this study. These data are inadequate to satisfy the requirements for reregistration because geographic representation is inadequate. Additional field residue data conducted in major onion-growing states other than CA and NY must be submitted. The following additional data are required:

- Revised labels specifying a maximum application rate of 2.4 lb ai/A/application, a maximum of 10 applications or 24 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 7 days. Application to exposed bulbs will be prohibited.

- Data depicting mancozeb, ETU, and other residues of concern in or on dry bulb onions harvested 7 days following the last of 10 foliar applications of a representative WP formulation at a maximum application rate of 2.4 lb ai/A applied at 7-day intervals. Tests must be conducted in CO(11%) and CA(32%); these states

along with TX(8%) and NY(6%) where data are available accounted for ca. 70% of the 1988 U.S. onion production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA, June 1989, p. 14).

References (used):

MRID(s): 40869708. 41092003.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40869708 and 41092003) submitted data from two tests conducted in CA and NY pertaining to residues of mancozeb and ETU in or on dry bulb onions harvested 0, 7, and 14 days following the last of 10 foliar applications (using ground equipment) of the 80% WP formulation at 2.4 lb ai/A/application (1x the maximum single and seasonal application rates allowed by PD 4). The results of the tests are presented in the following table.

Location	PTI (days)	Residues (ppm)[a] Mancozeb (Range)	ETU (Range)	Max. Storage (days)
CA	0	0.845-0.924	0.052-0.336	360
CA	7	<0.05-0.052	0.017-0.028	360
CA	14	<0.05	<0.05	360
NY	7	0.068-0.051	0.013-0.017	44

[a] Reported minimum-maximum values reflect duplicate analyses on a single sample from each harvest interval.

Apparent residues of mancozeb were <0.05(ND) ppm and of ETU were <0.01(ND) ppm in or on two untreated samples. Reported values were corrected for the average method recovery. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 93 and 94% from two samples fortified with mancozeb at 0.1 and 0.5 ppm, and 74-97% from three samples fortified with ETU at 0.01-0.1 ppm. Samples were stored frozen for 37-350 days prior to analysis for mancozeb and for 44-360 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability data were submitted to support this study. Based on potato storage stability data, residues of ETU would be expected to be stable for only 2 weeks of frozen storage.

Geographic representation is inadequate, since the test states of CA(32%) and NY(6%) accounted for only 38% of the 1988 U.S. onion

production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA, June 1989, p. 14). These data indicate that residues of mancozeb in or on two samples of dry bulb onions were below the established 0.5 ppm tolerance when harvested 7 days (the established PHI) following the last of 10 foliar applications of the 80% WP formulation at 2.4 lb ai/A/application (1x the maximum single and seasonal application rates allowed by PD 4). No concurrently conducted storage stability data were submitted to support this study. These data however, are inadequate to satisfy the requirements for reregistration because geographic representation is inadequate, and the CA samples were stored much longer than ETU is likely to remain stable in frozen storage. Data discussed in the Residue Chemistry Chapter where the use pattern matches that required by the PD 4 are available from FL and OH. Together with TX and neighboring states, these states represent only about 18% of US Onion production. Additional field residue data conducted in major onion-growing states other than TX and NY are required.

Fruiting Vegetables (Except Cucurbits) Group

Tomatoes

Tolerance(s):

A tolerance of 4 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on tomatoes [40 CFR §180.176].

Use directions and limitations:

The 32, 37, and 80% FlC, 70 and 75% DF, and 48, 62, 70 and 80% WP formulations are registered for multiple foliar applications at 3- to 14-day intervals to tomatoes at 1-2.4 lb ai/A/application using ground and aerial equipment. A 5-day PHI has been established. The FlC, DF, and WP formulations are also registered for seed treatment at 0.3-0.4 lb ai/100 lb seeds. No limit on the number of applications/season or maximum seasonal rate has been established except for the 48% WP (EPA Reg. No. 100-629) and 70% WP formulations (EPA Reg. No. 100-689). A maximum of four applications/season totalling 4 lb ai/A and a maximum of 22.4 lb ai/A/season are specified for the 48% and 70% WP formulations, respectively. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for tomatoes grown west of the Mississippi River must be revised to

specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 4 applications or 6.4 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days. All labels bearing use directions for tomatoes grown east of the Mississippi River must be revised to specify a maximum application rate of 2.4 lb ai/A/application, a maximum of 7 applications or 16.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data depicting residues in or on tomatoes harvested following applications (using ground and aerial equipment) of the WP and D formulations. In addition, the Guidance Document required revised labels specifying the maximum seasonal rate or the maximum number of applications/season.

The earlier tomato residue data discussed in the Residue Chemistry Chapter were inadequate because of lack of aerial data and the formulation used in older studies was not identified. Additionally, the tolerance might be inadequate. Although not mentioned in the conclusions, information on length and conditions of sample storage was also lacking.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRIDs 40869713 and 40869714 under CBRS No. 7959; and MRID 41844801) pertaining to residues of mancozeb and ETU in or on tomatoes. In addition, the Maneb Task Force submitted data (MRID 41901102 under CBRS No. 8636) pertaining to residues of mancozeb and ETU in or on tomatoes following treatment with mancozeb as part of a maneb data submission.

The submitted data (MRIDs 40869713 and 40869714) indicate that residues of mancozeb exceeded the established 4 ppm tolerance (up to 5.5 ppm) in or on four samples of tomatoes harvested 5 days following treatment at 1.5x the maximum single application rate, or 1.5-3x the maximum seasonal application rate allowed by PD 4 for tomatoes grown west of the Mississippi River. Additional data (MRID 41844801), with limited number of samples (2), reflecting treatments at 1x indicate that the established tolerance will not be exceeded. The available data however, do not fulfill the requirements for reregistration because no data were submitted reflecting the maximum use pattern allowed by PD 4 for tomatoes grown east of the Mississippi River. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 4 applications or 6.4 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days for tomatoes grown west of the Mississippi River. Revised labels specifying a

maximum application rate of 2.4 lb ai/A/application, a maximum of 7 applications or 16.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days east of the Mississippi River.

- Data depicting mancozeb, ETU, and other residues of concern in or on tomatoes harvested 5 days following the last of seven applications of a representative WP or FlC formulation at 2.4 lb ai/A/application at 7-day intervals. Tests on tomatoes must be conducted in states east of the Mississippi River, where this use pattern is allowed (FL(50%)).

The Mancozeb Guidance Document, dated 4/87, did not require additional processing studies for tomatoes. Data from a processing study previously reviewed in the Mancozeb Residue Chemistry Chapter indicated that mancozeb residues did not concentrate in processed tomato products, and that food/feed additive tolerances for these items are not needed. Data from the same study indicated that mancozeb residues degraded to ETU in juice, dry pomace, puree, and catsup.

The Mancozeb Task Force submitted additional processing data (MRID 40768001) which indicate that residues of mancozeb did not concentrate in the processed commodities of tomatoes. Apparent degradation to ETU residues occurred in some processed products. No additional processing data are required.

References (used):

MRID(s): 40768001. 40869713. 40869714. 41844801. 41901102.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40869713 and 40869714) submitted data from five tests conducted in CA pertaining to residues of mancozeb and ETU in or on tomatoes harvested 0-10 days following the last of four to eight applications of the 80% WP formulation at 2.4 lb ai/A/application (1.5x the maximum single application rate, 1.5-3x the maximum seasonal application rate allowed by PD 4 for tomatoes grown west of the Mississippi River). The results of the tests are presented below.

PTI	No. of Applns. = Total Rate (lb ai/A)	Residues (ppm)[a] Mancozeb (Range)	ETU (Range)	Max. Storage (days)
0	4 = 9.6	7.8-8.6(2)	0.03-0.16(2)	101
2	6 = 14.4	2.1-2.4(2)	<0.01-0.01(2)	101
2	8 = 19.2	1.0-10.0(4)	0.01-0.05(4)	101
3	7 = 16.8	3.0-3.5(2)	0.01 (2)	
5	4 = 9.6	4.7-5.1(2)	0.03-0.06(2)	329
5	6 = 14.4	1.3-1.6(2)	<0.01 (2)	101
5	8 = 19.2	0.7-5.5(4)	<0.01-0.03	101
10	4 = 9.6	3.2-3.4(2)	0.04-0.6(2)	329

[a] Reported residue values are corrected for average method recovery; the number of samples is given in parentheses.

Four samples harvested 5 days following the last of four or eight applications bore tolerance exceeding (4.7-5.5 ppm) residues of mancozeb. The samples with tolerance exceeding residues were treated at an exaggerated rate, compared to the rate allowed by PD 4.

Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on five untreated samples. Analyses were conducted using a modified colorimetric method (Keppel, Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 93-99% from six samples fortified with mancozeb at 0.05-12 ppm, and 82-100% from four samples fortified with ETU at 0.01-0.05 ppm. Samples were stored frozen (-10 C) for 101-324 days prior to analysis for mancozeb and for 97-329 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. Storage stability data reflecting these storage conditions and intervals are available to support this study; see "STORAGE STABILITY DATA" section.

The Mancozeb Task Force (1990; MRID 41844801 under CBRS No. 7959) submitted data from one test conducted in CA pertaining to residues of mancozeb and ETU in or on tomatoes harvested 4 and 10 days following the last of four applications of the 80% WP formulation at 2.4 lb ai/A/application (1.5x the maximum single and seasonal application rates allowed by PD 4 for tomatoes grown west of the Mississippi River). The results of the test are presented below.

PTI	No. of Applns. = Total Rate (lb ai/A)	Residues (ppm)[a] Mancozeb	ETU	Max. Storage (days)
4	4 = 9.6	1.38,1.40(2)	<0.003,0.005(2)	766
10	4 = 9.6	0.644(2)	<0.003,0.003(2)	760
--	untreated	<0.015(1)	<0.003(1)	770

[a] Reported residue values are corrected for average method recovery; the number of samples is given in parentheses.

Mancozeb analyses were conducted using a colorimetric method (PAM Vol. II, Method II) with a limit of detection of 0.015 ppm. ETU analyses were conducted using a GLC/FPD method (Onley, JAOAC 54:528-532) with a limit of detection of 0.003 ppm. Recoveries were 89% and 94% from two samples fortified with 0.05 and 1 ppm of mancozeb, respectively, and 74% and 109% from two samples fortified with 0.01 and 0.025 ppm of ETU, respectively. Samples were stored frozen (-10 C) for 738-770 days prior to analysis by Enviro-Bio-Tech, Ltd., Ltd. Storage stability data reflecting these storage conditions and intervals are available to support this study; however, the data indicate that residues of ETU are only stable up to one year in tomatoes; see "STORAGE STABILITY DATA" section of this document). Complete sample histories were not provided for all samples.

The Maneb Task Force (1991; MRID 41901102 under CBRS No. 8636) submitted data, as part of a maneb data submission, from eight tests conducted in CA depicting residues of mancozeb and ETU in or on tomatoes harvested 5-7 days following the last of one to four foliar applications (using ground and aerial equipment) of the 80% WP formulation at 2 lb ai/A/application (1.25x the maximum single application rate, 0.3-1.25x the maximum seasonal application rate allowed by PD 4 for tomatoes grown west of the Mississippi River). Residues of mancozeb were 0.084-3.72 ppm in or on 14 samples harvested five days following the last of four applications and <0.05(ND)-1.24 ppm in or on 14 samples harvested 7 days following a single application. Residues of ETU were <0.01(ND)-0.038 ppm in or on 14 samples harvested 5 days following the last of four applications and <0.01(ND) ppm in or on 14 samples harvested 7 days following a single application.

Mancozeb analyses were conducted by Morse Laboratories, Inc. using a GLC method (Morse Analytical Method No. MTF-88AM-005) with a limit of detection of 0.05 ppm. ETU analyses were conducted using an HPLC method (Morse Analytical Method No. MTF-88AM-004) with a limit of detection or 0.01 ppm. Residue results were corrected for average method recoveries of 94% for mancozeb and 77% for ETU. Recoveries were 84-108% from 12 tomato samples

fortified with mancozeb at 0.05-10 ppm; recoveries were 59-92% from 18 tomato samples fortified with ETU at 0.01-0.5 ppm. Samples were stored frozen (-20 C) for 30-170 days prior to analysis for mancozeb and 43-180 days prior to analysis for ETU. Storage stability data reflecting these storage conditions and intervals are available to support this study; see "STORAGE STABILITY DATA" section.

The Mancozeb Task Force (1990; MRID 40768001) submitted data from two tests conducted in PA pertaining to residues of mancozeb and ETU in the processed products of tomatoes harvested 5 or 11 days following the last of six foliar applications (using ground equipment) of the 37% FlC formulation at 2.4 lb ai/A. Unwashed tomatoes were processed according to commercial practices into washed tomatoes, tomato concentrate, juice, wet pomace, tomato sauce, and ketchup. The study was submitted because an earlier processing study did not reflect commercial practice with regard to the initial washing of tomatoes. Residues (corrected for method recovery) of mancozeb and ETU, mancozeb reduction factors, and conversion factors to ETU in the processed products of tomatoes are presented in the following table.

Commodity	No. of samples	Residues (ppm) Mancozeb[a]	ETU[a]	Minimum Reduction Factor[b]	Maximum % Conv. to ETU[c]
Whole tomatoes, unwashed	12	0.28-1.4	<0.01		
Whole tomatoes, washed	48	<0.05-0.08	<0.01-0.02	0.06	4%
Concentrate	12	<0.05	<0.01-0.05		14%
Juice	12	<0.05	0.02-0.04		11%
Wet pomace	12	<0.05	<0.01-0.02		4%
Sauce	3	<0.05-0.07	<0.01	0.05	
Ketchup	3	<0.05-0.06	<0.01-0.02	0.04	4%

[a] Reported values for residues were corrected for method recovery using 81% for mancozeb and ETU for the unwashed tomatoes and tomato sauce, and 95% for mancozeb and 96% for ETU for all other processed commodities.
[b] Reduction factors are obtained by dividing the residue in each processed commodity by the residue in or on the whole tomato.
[c] % Conversion = ETU residues in processed commodity minus ETU residue in raw commodity divided by the mancozeb residue concentration in the RAC.

Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on a single untreated washed tomato sample. Mancozeb analyses were conducted using a colorimetric method (No. TM-1853-1) with a limit of detection of

0.05 ppm. ETU analyses were conducted using a GLC method with a limit of detection of 0.01 ppm. Recovery of mancozeb and ETU from fortified samples is presented in the following table. Samples were stored for 7-33 days prior to analysis for mancozeb and for 14-40 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability data were submitted to support this study.

	Mancozeb			ETU		
Commodity	No. samples	Fort. level	% Recovery	No. samples	Fort. level	% Recovery
Whole fruit, washed	14	0.05-0.5	74-101	13	0.04-0.6	65-105
Concentrate	2	0.05	77	2	0.12, 0.25	102, 131
Juice	2	0.05	93, 110	--[a]	--	--
Wet pomace	2	0.05	77, 99	1	0.2	88
Sauce	1	0.25	82	2	0.05	79
Ketchup	1	0.15	87	4	0.05-1.2	74-87

[a] Indicates no data submitted.

Geographic representation of data reflecting use patterns allowed by PD 4 for tomatoes grown west of the Mississippi River is adequate since tests were conducted in CA which accounted for ca. 80% of the 1988 U.S. tomato production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA June 1989, pp. 16 and 43). The submitted data (MRIDs 40869713 and 40869714) indicate that residues of mancozeb exceeded the established 4 ppm tolerance (up to 5.5 ppm) in or on four samples of tomatoes harvested 5 days following treatment at 1.5x the maximum single application rate, or 1.5-3x the maximum seasonal application rate allowed by PD 4 for tomatoes grown west of the Mississippi River. Additional data (MRID 41844801), with limited number of samples (2), reflecting treatments at 1x indicate that the established tolerance will not be exceeded. The available data however, do not fulfill the requirements for reregistration because no data were submitted reflecting the maximum use pattern allowed for tomatoes grown east of the Mississippi River. Additional field residue data are required.

The submitted processing data (MRID 40768001) indicate that residues of mancozeb did not concentrate in the processed commodities. Apparent degradation to ETU residues occurred in some processed products. No additional processing data are needed.

Cucurbit Vegetables Group

Cucumbers

Tolerance(s):

A tolerance of 4 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on cucumbers [40 CFR §180.176].

Use directions and limitations:

The 70 and 80% WP, 32 and 37% FlC, 70% and 75% DF formulations are registered for multiple foliar applications to cucumbers at 1.5-2.4 lb ai/A/application using ground or aerial equipment. Applications may begin at the 2-leaf stage and be repeated at 5- to 7-day intervals. A 5-day PHI has been established. A maximum seasonal rate of 19.6 lb ai/A has been established for the 70% WP formulation (EPA Reg. No. 100-689); no maximum seasonal rate or maximum number of applications per season have been established for other products. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for cucumbers must be revised to specify a maximum application rate of 2.4 lb ai/A/application, a maximum of 8 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required data depicting residues in or on cucumbers harvested following application of WP and D formulations using ground and aerial equipment in separate tests. In addition, the Guidance Document required proposed label amendments specifying a maximum number of applications per season or a maximum seasonal rate.

The earlier cucumber residue data discussed in the Residue Chemistry Chapter were inadequate because of inadequate geographic representation and lack of information on length and conditions of sample storage. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Cucumber samples from 1985 tests were stored under unspecified conditions 1 to 133 days before analysis for mancozeb and 91 to 133 days before analysis for ETU.

Trials from FL and OH were conducted using the PD 4 use pattern. Residues were within tolerance.

In response to the Guidance Document, the Mancozeb Task Force submitted field residue data (MRIDs 40869707 and 41092006) from tests conducted in CA, GA, and TX. Only data from TX was conducted according to the use patterns allowed by PD 4. Data from TX indicate that mancozeb residues will not exceed the established tolerance of 4 ppm in or on cucumbers when treated with WP formulation at 1x the maximum single application rate, or 1.1x the maximum seasonal application rate. The available data do not fulfill the requirements for reregistration because geographic representation is inadequate. The following additional data are required:

- Revised labels specifying a maximum application rate of 2.4 lb ai/A/application, a maximum of 8 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days.

- Data depicting mancozeb, ETU, and other residues of concern in or on cucumbers harvested 5 days following the last of 8 foliar applications of a representative WP or FlC formulation at a maximum application rate of 2.4 lb ai/A applied at 7-day intervals. Tests must be conducted in CA (11%) and NC(15%); these states along with TX(8%) and OH(6%) and neighboring states of MI(19%) and WI(7%), where data are available, accounted for ca. 70% of the 1988 cucumber production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA Crop Database, June 1989, p. 40).

References (used):

MRID(s): 40869707. 41092006.

Discussion of the data:

The Mancozeb Task Force (1986; MRID 408697071987; and MRID 41092006) submitted data from four tests conducted in CA(1), GA(2), and TX(1) pertaining to residues of mancozeb and ETU in or on cucumbers harvested 0-10 days following the last of 3-7 foliar applications with the 80% WP and the 37% FlC formulations using ground equipment at 1.6-2.4 lb ai/A/application (0.7-1x the maximum single application rate, or 0.4.-1.1x the maximum seasonal application rate allowed by PD 4). The results of these tests are presented below.

Site	PTI (days)	No. of Applns. = rate[b]	Residues (ppm)[a] Mancozeb (Range)	ETU (Range)	Maximum Storage (days)
CA	5	3(2.4) = 7.2	0.11	0.03-0.05	418
TX[c]	**5**	**9(2.4) = 21.6**	**0.08-0.10**	**0.04-0.05**	**418**
GA[d]	0	7(1.6) = 11.2	1.38-1.59	0.02	553
	10	7(1.6) = 11.2	0.43-0.55	<0.01-0.01	553
GA	0	7(1.6) = 11.2	0.87-1.04	0.03-0.04	553
	10	7(1.6) = 11.2	0.47-0.53	<0.01-0.02	553

[a] Residue values were corrected for average method recovery of 90%(GA), 98%(TX), and 96%(CA) for mancozeb; and 99%(GA), 85%(TX), and 94%(CA) for ETU. Minimum-maximum ranges reflect two samples. [b] Rates are in lb ai/A.
[c] Row in bold represents use pattern allowed by PD 4.
[d] The 37% FlC formulation was used in this test.

Apparent residues of mancozeb and ETU were <0.05 ppm (ND) and <0.01 ppm (ND), respectively, in or on three untreated samples; one additional untreated sample from a GA test bore mancozeb and ETU residues of 1.1 and <0.01 ppm (ND), respectively. Analyses were conducted by Enviro-Bio-Tech, Ltd., using a colorimetric method (Keppel) for mancozeb with a limit of detection of 0.05 ppm, and a GLC method (Onley) for ETU with a limit of detection of 0.01 ppm. Recoveries were 89-98% from four samples fortified with mancozeb at 0.1-2 ppm, and was 85-100 from four samples fortified with ETU at 0.01-0.04 ppm. Samples from TX and CA tests were stored for 389-413 days prior to analysis for mancozeb and for 396-418 days prior to analysis for ETU. Samples from GA tests were stored for 553 days prior to analysis for mancozeb and for 496 days prior to analysis for ETU. No concurrently conducted storage stability data were submitted to support this study. Earlier tomato storage stability studies indicated that mancozeb was stable up to 2 years and ETU up to one year in frozen storage. Recovery of ETU was 58% after 2 years in frozen storage.

Data from FL and OH, reflecting the PD 4 use pattern were discussed in the Residue Chemistry Chapter. Residues were within tolerance.

Geographic representation of <u>adequate data</u> is lacking since only the study from TX and earlier studies from OH and FL were conducted according to the use patterns allowed by PD 4. The test state of TX accounted for only 8% of the 1988 cucumber production (<u>Vegetables</u>, 1988 Summary, Ag. Statistics Board, NASS, USDA Crop Database, June 1989, p. 40). Data from TX indicate that mancozeb residues will not exceed the established tolerance of 4 ppm in or on cucumbers when treated at 1x the maximum single

application rate, or 1.1x the maximum seasonal application rate. Additional field residue data from major cucumber-growing regions are required.

Pome Fruits Group

Apples

Tolerance(s):

A tolerance of 7 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on apples [40 CFR §180.176].

Use directions and limitations:

The 80% WP, 32% FlC, 70% and 75% DF formulations are registered for multiple foliar applications to apples at 6.4-8 lb ai/A (0.8-1.6 lb ai/100 gal water) using ground or aerial equipment. Application may be made at green tip or delayed dormant stage, and repeated at 7- to 14-day intervals. A 21-day PHI has been established in AL, AR, DE, GA, IL, IN, KS, KY, MD, MO, NC, NJ, OH, PA, SC, TN, VA, and WV; a 30-day PHI has been established in all other states. Livestock may not be grazed in treated orchards. No maximum number of applications per season or a maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for apples must be revised to specify that the product may be used with either the pre-bloom use pattern or the extended application use pattern and that these two treatment schedules must not be combined or integrated. For the pre-bloom use pattern, the labels must specify a maximum application rate of 4.8 lb ai/A, a maximum of four applications or 19.2 lb ai per season, an application interval of 7 to 10 days, and a minimum preharvest interval to bloom. For the extended application use pattern, the labels must specify a maximum application rate of 2.4 lb ai/A, a maximum of seven applications or 16.8 lb ai per season, an applications interval of 7 to 10 days, and a minimum PHI of 77 days. Additionally, labels must state that use is recommended within an IPM program.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required data depicting residues in or on apples harvested 21 or 30 days following multiple foliar applications of the WP or F1C and the D formulations. The Guidance Document required the registrant(s) to propose label revisions and submit ETU residue data for all apple samples stored ≥6 months. In addition, the Guidance Document required a proposal for a feed additive tolerance for mancozeb residues in dry pomace, based on a 13x concentration factor. According to the EPA Site Listing (SPO5) dated 9/25/90, all D formulation uses on apples have been canceled.

In response to the Guidance Document, Mancozeb Task Force submitted field residue data (MRID 41092007) from tests conducted in NY and WA pertaining to residues of mancozeb and ETU in or on apples. The available data from the WA test site indicate that residues of mancozeb in or on apples harvested 30 days following treatments at 2.7x the maximum single application rate, or 1.5x the maximum seasonal application rate allowed by PD 4 for the "extended use pattern", were below the established tolerance of 7 ppm. Residues of ETU were 0.22-0.24 ppm in or on these same samples. The submitted field residue data, however, do not fulfill the requirements for reregistration because apples were not analyzed within the time interval that ETU residues remain stable (one month). Apple samples were stored frozen for 34-427 days prior to analysis for mancozeb and for 39-432 days prior to analysis for ETU. Storage stability data reflecting these storage intervals and conditions indicate that residues of mancozeb in or on apples are stable for up to 24 months; residues of ETU however, are only stable for up to one month.

The EBDC/ETU Task Force submitted additional residue data on apples reflecting early season use (MRID 41731801) and "second cover use with 77-day PHI" (MRIDs 41831501 and 42036901). These data were submitted in response to the Special Review Data Call In Notice of 11/7/90 to support the possibility of use patterns with longer preharvest interval and reduced application rates. The submissions were reviewed by S. Hummel (CBRS No. 7499 dated 5/23/91 and CBRS No. 8750 dated 1/8/92) who concluded that these data will not be sufficient for continued reregistration of apples because of inadequate geographical representation; only one location per state was tested.

The following additional data are required:

- Revised labels specifying that the product may be used with either the pre-bloom use pattern or the extended application use pattern and that these two treatment schedules must not be combined or integrated. For the pre-bloom use pattern, the labels must specify a maximum application rate of 4.8 lb ai/A, a maximum of four

applications or 19.2 lb ai per season, an application interval of 7 to 10 days, and a minimum preharvest interval to bloom. For the extended application use pattern, the labels must specify a maximum application rate of 2.4 lb ai/A, a maximum of seven applications or 16.8 lb ai per season, an application interval of 7 to 10 days, and a minimum PHI of 77 days. Additionally, labels must state that use is recommended within an IPM program. Grazing of livestock in treated areas must be prohibited. Aerial application is allowed in a minimum spray volume of 10 gal/A.

- Data depicting mancozeb, ETU, and other residues of concern in or on apples reflecting the pre-bloom and extended application use patterns (in separate tests). For prebloom use pattern, apples must be harvested at bloom after the last of 4 applications of a representative WP or FlC formulation at 4.8 lb ai/A/application made at 7-day intervals. For extended application use pattern, apples must be harvested 77 days after the last of 7 applications per season of a representative WP or FlC formulation at 2.4 lb ai/A/application made at 7-day intervals. Tests must be conducted in WA(43%), NY(10%)/PA(6%), MI(9%), and VA(5%)/NC(4%), since these states accounted for 77% of the 1988 U.S. apple production (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

- An appropriate level for the feed additive tolerance for mancozeb residues in dry apple pomace will be determined when the adequacy of the tolerance for residues in or on apples is assessed, following receipt of the requested field data.

References (used):

MRID(s): 41092007. 41731801. 41831501. 42036901.

Discussion of the data:

The Mancozeb Task Force (1988; MRID 41092007) submitted data from two tests conducted in NY and WA pertaining to residues of mancozeb and ETU in or on apples harvested 30 days following the last of 4-10 foliar applications with the 80% WP formulation using ground equipment at 6.4-8 lb ai/A/application (2.7-3.3x the maximum single application rate, or 1.5-5.2x the maximum seasonal application rate allowed by PD 4 for the "extended use pattern"). The results of these tests are presented below.

Site	PTI (days)	No. of Applns. = rate[b]	Residues (ppm)[a] Mancozeb (Range)	ETU (Range)	Max. Storage (days)
WA	30	4(6.4) = 25.6	5.3-6.4	0.22-0.24	427
NY	30	10(8.0) = 80.0	9.2	0.15-0.16	427

[a] Residue values were corrected for average method recovery of 94%(WA) and 96%(NY) for mancozeb; and 88%(WA) and 92%(NY) for ETU. Ranges reflect two samples.
[b] Rate in lb ai/A.

Apparent residues of mancozeb and ETU were <0.05 ppm (ND) and <0.01 ppm (ND), respectively, in or on two untreated samples. Analyses were conducted by Enviro-Bio-Tech, Ltd., using a colorimetric method (Keppel) for mancozeb with a limit of detection of 0.05 ppm, and a GLC method (Onley) for ETU with a limit of detection of 0.01 ppm. Recoveries were 94 and 96% from two samples fortified with mancozeb at 6 and 10 ppm, and was 82-100% from four samples fortified with ETU at 0.01-0.4 ppm. Samples were stored for 34-427 days prior to analysis for mancozeb and for 39-432 days prior to analysis for ETU. Storage stability data reflecting these storage intervals and conditions are available; see "STORAGE STABILITY DATA" section. These data indicate that residues of mancozeb in or on apples are stable for up to 24 months; residues of ETU are only stable for up to one month.

Geographic representation for apples is adequate since the test states of NY(10%) and WA(43%) and the neighboring states of CT(1%), ID(1%), MA(1%), NJ(1%), OR(2%), and PA(6%) collectively accounted for ca. 70% of the 1988 apple production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data from the WA test site indicate that residues of mancozeb in or on apples harvested 30 days following treatments at 2.7x the maximum single application rate, or 1.5x the maximum seasonal application rate allowed by PD 4 for the "extended use pattern", were below the established tolerance of 7 ppm. Residues of ETU were 0.22-0.24 ppm in or on these same samples. The submitted field residue data, however, do not fulfill the requirements for reregistration because data are not supported by storage stability data; apples were not analyzed within the time interval that ETU residues remain stable (one month). Additional data are required.

Pears

Tolerance(s):

A tolerance of 10 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on pears [40 CFR §180.176].

Use directions and limitations:

The 80% WP, 32 and 37% FlC, 70% and 75% DF formulations are registered for use on pears for multiple foliar applications at 6.4-8 lb ai/A (1.2 lb ai/100 gal water). Pear trees may also be sprayed postharvest at 1.2-1.6 lb ai/100 gal water (with up to 1,000 gal of finished spray/A). Applications may be made at green tip or delayed dormant stage, and repeated at 7- to 14-day intervals. Foliar applications may be made using both ground and aerial equipment. A 15-day PHI has been established. Livestock may not graze on treated areas. No maximum number of applications per season or a maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for pears must be revised to specify that the product may be used with either the pre-bloom use pattern or the extended application use pattern and that these two treatment schedules must not be combined or integrated. For the pre-bloom use pattern, the labels must specify a maximum application rate of 4.8 lb ai/A, a maximum of four applications or 19.2 lb ai per season, an application interval of 7 to 10 days, and a minimum preharvest interval to bloom. For the extended application use pattern, the labels must specify a maximum application rate of 2.4 lb ai/A, a maximum of seven applications or 16.8 lb ai per season, an applications interval of 7 to 10 days, and a minimum PHI of 77 days. Additionally, labels must state that use is recommended within an IPM program.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required data depicting residues in or on pears harvested following multiple foliar applications of the WP and D formulations using ground and aerial equipment in separate tests. In addition, the Guidance Document required the registrant(s) to propose label revisions specifying the number of applications per season and the maximum seasonal use rate. According to the EPA Site Listing (SPO5)

dated 9/25/90, all D formulation uses on pears have been canceled.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRID 40913306). These data indicate that residues of mancozeb were below the established tolerance of 10 ppm in or on pears harvested 7-21 days following the last of six applications of the 80% WP formulation at 2.7x the maximum single application rate, or 2.3x the maximum seasonal application rate allowed by PD 4 for the "extended use pattern"; residues of ETU were up to 0.06 ppm from these same samples. No concurrently conducted storage stability data were submitted to support this study.

The Mancozeb Task Force also submitted supplementary information (1988; MRID 40913305) for a previously reviewed submission (MRID 40128801) discussed in the Mancozeb Residue Chemistry Chapter, dated 9/86. This submission clarifies the application rate as 1.6 lb ai/100 gal rather than 1.6 lb ai/A as reported in the Science Chapter. Data from the two CA tests reported remains inadequate because no data were submitted depicting the conditions or duration of storage of the samples prior to analysis.

The available data do not fulfill the requirements for reregistration because geographic representation of data reflecting the "extended use pattern" is inadequate, and no data reflecting the "prebloom use pattern" have been submitted. The following additional data are required:

- Revised labels specifying a maximum prebloom application rate of 4.8 lb ai/A/application, a maximum of 4 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of bloom; and a maximum extended application rate of 16.8 lb ai/A/application, a maximum of 7 applications or 16.8 lb ai/A/season, a minimum application interval of 7 days, and a PHI of 77 days. Grazing of livestock in treated areas must be prohibited. Aerial application is allowed with a minimum spray volume of 10 gal/A.

- Data depicting mancozeb, ETU, and other residues of concern in or on pears reflecting the pre-bloom <u>and</u> extended application use patterns (in separate tests). For prebloom use pattern, pears must be harvested at bloom after the last of 4 applications of a representative WP or FlC formulation at 4.8 lb ai/A/application made at 7-day intervals. For extended application use pattern, pears must be harvested 77 days after the last of 7 applications per season of a representative WP or FlC formulation at 2.4 lb ai/A/application made at 7-day intervals. Tests must be

conducted in CA(35%) and WA(36%) since these states accounted for ca. 70% of the 1988 pear production (Ag. Statistics Board, NASS, USDA, Aug. 1989).

References (used):

MRID(s): 40913305. 40913306.

Discussion of the data:

The Mancozeb Task Force (1985; MRID 40913306) submitted data from one test conducted in PA pertaining to residues of mancozeb and ETU in or on pears following six foliar applications (using ground equipment) of the 80% WP formulation at 6.4 lb ai/A (2.7x the maximum single application rate, or 2.3x the maximum seasonal application rate allowed by PD 4 for the "extended use pattern"). The results of this test are presented below.

PTI (days)	No. of Applns. = rate[b]	Residues (ppm)[a] Mancozeb (Range)	ETU (Range)
7	6(6.4) = 38.4	4.9-5.3	0.05
14	6(6.4) = 38.4	4.0-4.4	0.05-0.06
21	6(6.4) = 38.4	2.6-2.8	0.05

[a] Residue values were corrected for average method recovery of 95% for mancozeb; and 88% ETU. Ranges reflect two samples.
[b] Rate in lb ai/A.

Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on one untreated sample. Analyses were conducted by Enviro-Bio-Tech, Ltd., using a colorimetric method (Keppel) for mancozeb with a limit of detection of 0.05 ppm, and a GLC method (Onley) for ETU with a limit of detection of 0.01 ppm. Recoveries were 94-96% from three samples fortified with mancozeb at 0.05-6 ppm, and 100% from one sample fortified with ETU at 0.05 ppm. Samples were stored for 108-122 days prior to analysis for mancozeb and for 383-397 days prior to analysis for ETU. No concurrently conducted storage stability data were submitted to support this study. Earlier frozen storage stability studies on apples indicated that ETU was stable only three months in frozen storage.

Geographic representation of data reflecting "extended use pattern" is inadequate since the test state of PA(<1%) and the neighboring state of NY(2%) collectively accounted for <3% of the 1988 pear production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The submitted data indicate that residues of mancozeb were below the established tolerance of 10 ppm in or

on pears harvested 7-21 days following the last of six applications of the 80% WP formulation at 2.7x the maximum single application rate, or 2.3x the maximum seasonal application rate allowed by PD 4 for the "extended use pattern"; residues of ETU were up to 0.06 ppm from these same samples. No concurrently conducted storage stability data were submitted to support this study.

The available data do not fulfill the requirements for reregistration because geographic representation of data reflecting the "extended use pattern" is inadequate, and no data reflecting the "prebloom use pattern" have been submitted. Additional data are required.

Small Fruits and Berries Group

Cranberries

Tolerance(s):

A tolerance of 7 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on cranberries [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered for multiple foliar applications to cranberries at 2.3-5 lb ai/A/application using ground or aerial equipment. Application may begin at midbloom and repeated at 7-10 day intervals. A 30-day PHI has been established. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for cranberries must be revised to specify a maximum application rate of 4.8 lb ai/A/application, a maximum of 3 applications or 14.4 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 30 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data depicting mancozeb and ETU residues in or on cranberries following multiple foliar application of the WP and 3.2% D

formulations using ground and aerial equipment in separate tests. The Guidance Document also required revised labels specifying the maximum seasonal rate or the maximum number of applications per season. According to the EPA Site Listing (SP05) dated 9/25/90, all D formulation uses on cranberries have been canceled.

The earlier cranberry residue data discussed in the Residue Chemistry Chapter were inadequate because of inadequate geographic representation and lack of information on length and conditions of sample storage. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Cranberry samples from 1985 tests were stored 80 to 137 days before analysis for mancozeb and 66 to 144 days before analysis for ETU. Based on apple storage stability data, ETU residues would only be expected to be stable for three months in frozen storage. Trials matching the PD 4 use pattern were available from WA, OR, and NJ.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRID 40869706) depicting residues of mancozeb and ETU in or on cranberries. The available data indicate that residues of mancozeb will not exceed the established 7 ppm tolerance in or on cranberries harvested 30 days following the last of four foliar applications of the 80% WP formulation at 1x the maximum single application rate allowed by PD 4. Residues of ETU up to 0.06 ppm were reported. The EBDC PD 4 only allows a maximum of three applications per season; the submitted data support the established tolerance for up to four applications per season. However, the submitted data do not satisfy requirements for reregistration because geographical representation is inadequate; the test state of MA(48%), along with NJ(9%), OR(4%)and WA(3%) represented only ca. 64% of the 1988 U.S. cranberry production. The following additional data are required:

- Revised labels specifying a maximum application rate of 4.8 lb ai/A/application, a maximum of 3 applications or 14.4 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 30 days.

- Data depicting mancozeb, ETU, and other residues of concern in or on cranberries harvested 30 days following the last of 3 foliar applications of a representative WP, FlC, or DF formulation at a maximum application rate of 4.8 lb ai/A applied at 7 day intervals. Tests must be conducted in WI(36%) since this state, along with MA(48%), NJ(9%), OR(4%), and WA(3%), where data are available, accounted for ca. 100% of the 1988 U.S. cranberry production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989).

References (used):

MRID(s): 40869706.

Discussion of the data:

The Mancozeb Task Force (1988; MRID 40869706) submitted data from a single study conducted in MA pertaining to residues of mancozeb and ETU in or on cranberries harvested 30 days following the last of four foliar applications (using ground equipment) of the 80% WP formulation at 4.8 lb ai/A (1x the maximum single application rate allowed by PD 4). Residues of mancozeb were 4.7 and 4.9 ppm, and residues of ETU were 0.06 ppm in or on two samples. Apparent residues of mancozeb and ETU were <0.05(nondetectable; ND) and <0.01(ND) ppm, respectively in or on one untreated sample. Reported residue values were corrected for method recovery. Mancozeb analyses were conducted using a modified colorimetric method (Keppel, Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 93% from one sample fortified with mancozeb at 5 ppm, and 76% from one sample fortified with ETU at 0.05 ppm. Samples were stored frozen (-10 C) for 31 days prior to analysis for mancozeb and for 33 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data; however, storage stability data pertaining to apples may be translated to support these data (see "STORAGE STABILITY DATA" section). Residues of ETU were stable for only three months of frozen storage.

Geographic representation is inadequate since the test state of MA accounted for only ca. 50% of the 1988 U.S. cranberry production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data indicate that residues of mancozeb were below the established 7 ppm tolerance in or on cranberries harvested 30 days following the last of four applications of the 80% WP formulation at 1x the maximum single application rate allowed by PD 4. Additional data are required.

Grapes

Tolerance(s):

A tolerance of 7 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on grapes [40 CFR §180.176].

A food additive tolerance of 28 ppm has been established for the same residues in raisins [40 CFR §185.6300].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered for multiple foliar applications to grapes at 0.93-3.2 lb ai/A/application using ground and aerial equipment. Treatments may be applied when shoots are 3-5 inches long, when shoots are 8-10 inches long, and then at 10-14 day intervals until fruit is set. A 66-day PHI has been established for areas other than CA; in CA application may not be made after fruit is set. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for grapes grown east of the Rocky Mountains must be revised to specify a maximum application rate of 3.2 lb ai/A/application, a maximum of 6 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 66 days. All labels bearing use directions for grapes grown west of the Rocky Mountains (except CA) must be revised to specify a maximum application rate of 2 lb ai/A/application, a maximum of 3 applications or 6 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 66 days. All labels bearing use directions for grapes grown in CA must be revised to specify a maximum application rate of 2 lb ai/A/application, a maximum of 3 applications or 6 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI such that no application may occur after bloom.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data depicting residues in or on grapes following multiple foliar applications of the WP and D formulations using ground and aerial equipment in separate tests. In addition, the Guidance Document required revised labels specifying the maximum seasonal application rate and establishing a PHI for mancozeb use in CA. The Guidance Document also required the registrant to propose food/feed additive tolerances for mancozeb residues in grape pomace (wet and dry), grape juice, and raisin waste.

The earlier grape residue data discussed in the Residue Chemistry Chapter were inadequate because the treatments did not reflect the maximum use pattern and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but

not the conditions of storage. Grape samples from 1983 to 1985 studies were stored 73 to 171 days before analysis for mancozeb and 71 to 227 days before analysis for ETU. Based on apple storage stability studies, ETU residues would be expected to be stable for three months in frozen storage.

In response to the Guidance Document, the Mancozeb Task Force submitted field data (MRIDs 41092001 and 41092002) pertaining to residues of mancozeb in or on grapes. The available data indicate that residues of mancozeb will not exceed the established tolerance in or on grapes harvested 66-100 days following 3-5 applications of the 80% WP formulation at 3.2 lb ai/A/application (1x the maximum single application rate allowed by PD 4; 0.5-0.8x the maximum seasonal application rate allowed by PD 4 east of the Rocky Mountains). Residues of ETU were <0.01(ND)-1.83 ppm in or on these same samples. These data do not satisfy the requirements for reregistration because no data were submitted reflecting treatment at 1x the maximum seasonal application rate allowed by PD 4 east of the Rocky Mountains. No concurrently conducted storage stability studies were submitted to support these data. The following additional field data are required:

- Revised labels specifying a maximum application rate of 3.2 lb ai/A/application, a maximum of 6 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 66 days for grapes grown east of the Rocky Mountains; and a maximum application rate of 2 lb ai/A/application, a maximum of 3 applications or 6 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 66 days for grapes grown west of the Rocky mountains, except for CA where no application is permitted after bloom.

- Data depicting mancozeb, ETU, and other residues of concern in or on grapes harvested 66 days following the last of 6 foliar applications of a representative WP, FlC, or DF formulation at maximum application rate of 3.2 lb ai/A applied at 7-day intervals. Tests must be conducted in NY since this state accounted for most of the 1988 U.S. production of grapes outside of CA (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

The Mancozeb Task Force (MRID 41483801) also submitted data pertaining to residues of mancozeb and ETU in the processed commodities of grapes. The available processing data indicate that residues of mancozeb concentrated up to 30x in raisin waste but did not concentrate in raisins, wet pomace, dry pomace, or juice. Residues were converted to ETU in juice (90% conversion) and raisin waste (34%). Data reviewed in the Mancozeb Residue Chemistry Chapter indicated concentration of residues up to 3x in

raisins, 5x in raisin waste, 3x in wet pomace, 20x in dry pomace, and 21x in juice. The registrant explained that the processing studies were done with unwashed grapes. Thus, the established food additive tolerance for mancozeb on raisins is not needed and should be revoked.

- Appropriate food/feed additive tolerances will be determined for the processed products of grapes when the adequacy of the tolerance for residues in or on grapes is assessed, following receipt of the required field data.

We note that Ciba-Geigy submitted data (MRID 41150101) to support the proposed use of their 48% WP formulation (Ridomil MZ58; EPA Reg. No. 100-629). These data were reviewed by the Agency (EPA Memoranda CBTS Nos. 5557 and 5558, G.F. Otakie, dated 12/11/89) who concluded the following: (i) residues in or on grapes treated using the proposed use were above the established tolerance; (ii) data are not valid since the samples were stored up to 20 months before analysis and storage stability data conducted concurrently at the same laboratory were not provided; and (iii) detailed information regarding the methods used in the processing studies and information regarding storage duration and condition from harvest to analysis for both raw and processed samples are required.

References (used):

MRID(s): 41092001. 41092002. 41150101. 41483801.

Discussion of the data:

The Mancozeb Task Force (1987; MRIDs 41092001 and 41092002) submitted data from eight studies conducted in CA(6), NY(1), and PA(1) pertaining to residues of mancozeb and ETU in or on grapes harvested 66-100 days following multiple foliar applications of the 80% WP formulation at 3.2 lb ai/A (1x the maximum single application rate allowed by PD 4) using ground equipment. Results of these tests are presented below.

Location	PHI (days)	No. of Applns. = rate[b]	Residues (ppm)[a] Mancozeb Range	ETU Range
CA	66	4(3.2) = 12.8	0.38-1.65(6)	<0.01-0.03(6)
	82	3(3.2) = 9.6	0.40-0.44(2)	<0.01-0.01(2)
	94	3(3.2) = 9.6	0.41-0.48(2)	<0.01(2)
	100	3(3.2) = 9.6	0.51-0.68(2)	<0.01-0.01(2)
NY	66	4(3.2) = 12.8	0.80-1.83(4)	0.01-0.04(4)
PA	66	5(3.2) = 16.0	0.41-0.50(4)	<0.01(4)

[a] Residue values were corrected for average method recovery of 93 or 94% for mancozeb and 82% for ETU. The number of samples in each range is given in parentheses.
[b] lb ai/A.

Apparent residues of mancozeb and ETU were <0.05 ppm (ND) and <0.01 ppm (ND), respectively in or on seven untreated samples. Mancozeb analyses were conducted using a modified colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 93-94% from seven samples fortified with mancozeb at 0.5-2.0 ppm, and were 65-112% from twelve samples fortified with ETU at 0.01-0.05 ppm. Samples were stored frozen (-10 C) for 52-114 days prior to analysis for mancozeb and for 64-148 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data. Based on older storage stability studies on apples, residues of ETU would be likely to be stable for three months in frozen storage.

The Mancozeb Task Force (1990; MRID 41483801) submitted data from a processing study conducted in CA pertaining to residues of mancozeb and ETU in or on grapes harvested 82 days following the last of three foliar applications of the 80% WP formulation at 3.2 lb ai/A/application (1x the maximum single application rate allowed by PD 4). One sample of grapes was processed into raisins, dry pomace, wet pomace, juice, and raisin waste according to simulated commercial procedures. Residues of mancozeb and ETU in or on grapes and in the processed products of grapes are presented in the table below.

Commodity	Residues (ppm)[a] Mancozeb	ETU	Conc. or Reduc. Mancozeb[b]	% Conv. to ETU[c]
Grapes	0.41	0.06	--	--
Juice	0.51	0.43	1.2	90
Dry Pomace	0.37	0.02	0.9	--
Wet Pomace	0.47	0.05	1.1	--
Grade AB raisins	0.09	<0.01	0.2	--
Grade C raisins	0.28	<0.01	0.7	--
Grade M raisins	0.34	<0.01	0.8	--
Grade S raisins	0.43	0.01	1.0	--
Raisin waste	12.3	0.2	30	34

[a] Reported values are the average of duplicate samples corrected for method recovery using 94% for mancozeb and 89% for ETU.
[b] Concentration or reduction factors are obtained by dividing the residue in each processed commodity by the residue in or on the RAC.
[c] Calculated as follows:
[(ETU product - ETU RAC)/Mancozeb RAC] x 100 = % Conversion.

Apparent residues of mancozeb and ETU were <0.05 ppm (ND) and <0.01(ND)-0.02 ppm, respectively, in one untreated sample of grapes and processed products. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Samples were stored frozen for 231 days prior to analysis for mancozeb and for 235-267 days prior to completion of analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data. Recoveries from samples fortified with mancozeb at 0.05-12 ppm and with ETU at 0.01 and 0.1 ppm are presented in the following table.

Commodity	Percentage Recovery Mancozeb	ETU
Grapes	89.2, 93.4	97, 81
Juice	94.4, 97.6	69.5, 123
Dry Pomace	89.2, 93.4	124, 75.9
Wet Pomace	84, 95.4	97.5, 89.8
Grade AB raisins	94.4, 89.2	91, 93.5
Grade C raisins	89.2, 91	81.5, 83.6
Grade M raisins	89.4, 95.6	91, 114
Grade S raisins	84, 94.4	60.5, 99.4
Raisin waste	84, 96.3	100, 89.1

Geographic representation is adequate since the test states of CA(92%), NY(3%), and PA(1%) accounted for 96% of the 1988 U.S. grape production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data indicate that residues of mancozeb will not exceed the established tolerance in or on grapes harvested 66-100 days following 3-5 applications of the 80% WP formulation at 3.2 lb ai/A/application (1x the maximum single application rate allowed by PD 4; 0.5-0.8x the maximum seasonal application rate allowed by PD 4). Residues of ETU were <0.01(ND)-1.83 ppm in or on these same samples. These data are inadequate to satisfy the requirements for reregistration because no data were submitted reflecting treatment at 1x the maximum seasonal application rate allowed by PD 4 east of the Rocky Mountains. No concurrently conducted storage stability studies were submitted to support these data. The available processing data indicate that residues of mancozeb concentrate up to 30x in raisin waste and that residues were converted to ETU in juice and raisin waste. Additional data are required.

Cereal Grains Group

Field corn

Tolerance(s):

A tolerance of 0.1 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on corn grain (except popcorn grain) [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered for multiple foliar applications to hybrid and field corn at 1.1-1.2 lb ai/A/application using ground or aerial equipment. Applications may be repeated as needed at 4-14 day intervals. A 40-day PHI has been established. The 80% WP, 32, 37, and 80% FlC, and 70% and 75% DF formulations are also registered for seed treatment of field corn at 0.13-0.27 lb ai/100 lb seed. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for field corn must be revised to specify a maximum application rate of 1.2 lb ai/A/application, a maximum of 10 applications or 12 lb ai/A/season, and a minimum PHI of 40 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required field data depicting residues in or on field corn following multiple foliar applications of the WP and D formulations made using ground and aerial equipment in separate tests. The Guidance Document required the registrant(s) to propose label revisions establishing a maximum seasonal use rate or maximum number of applications per season. In addition, the Guidance Document required a processing study.

The earlier residue data on field corn discussed in the Residue Chemistry Chapter were inadequate because information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Field corn samples were stored 97 to 622 days before analysis (most within 265 days of harvest). Data reflecting the PD 4 use pattern were available from FL. The field corn processing study was inadequate because samples bearing non-detectable residues were processed.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRID 40869705) pertaining to residues of mancozeb and ETU in or on field corn grain. The available field residue data indicate that residues of mancozeb will not exceed the established tolerance in or on field corn grain harvested 54 days following the last of seven applications of the 80% WP formulation at 1.2 lb ai/A/application (1x the maximum allowed single application rate allowed by PD 4; 0.7x the maximum seasonal application rate allowed by PD 4). Residues of ETU were <0.01(ND) ppm in or on these same samples. The available field residue data do not satisfy the requirements for reregistration because no data were submitted reflecting treatments made at 1x the maximum seasonal application rate or the minimum PHI allowed by PD 4. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, a maximum of 10 applications or 12 lb ai/A/season, and a minimum PHI of 40 days.

- Data depicting mancozeb, ETU, and other residues of concern in or on field corn grain harvested 40 days following the last of 10 applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A/application. Tests for field corn must be conducted in IA(18%), IL(14%), MN(7%), NE(17%), and OH(5%), since these states,

along with neighboring states of IN(8%), KS(3%), SD(3%), WI(3%), and MI(2%), accounted for ca. 80% of the 1988 corn grain production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989).

The Mancozeb Task Force also submitted data (MRID 41091701) pertaining to residues of mancozeb and ETU in the processed commodities of field corn. The available processing data are inadequate to determine the potential for concentration of mancozeb and ETU residues because the commodities were processed from field corn bearing nondetectable residues of mancozeb and ETU. In addition, no data were submitted for the wet milled products, crude oil and refined oil, or for grain dust.

The following additional data are required:

- A processing study depicting the potential for concentration of mancozeb, ETU, and other residues of concern in wet milled products (starch, crude oil, and refined oil) and in dry milled products (grits, meal, flour, and crude and refined oils) and grain dust from the processing of field corn bearing measurable, weathered residues. If residues concentrate/convert in any product, then appropriate food/feed additive tolerances must be proposed.

References (used):

MRID(s): 40869705. 41091701.

Discussion of the data:

The Mancozeb Task Force (1988; MRID 40869705) submitted data from one test conducted in HI pertaining to residues of mancozeb and ETU in or on field corn grain harvested 54 days following the last of seven foliar applications (using ground equipment) of the 80% WP formulation at 1.2 lb ai/A/application (1x the maximum single and 0.7x the maximum seasonal application rate allowed by PD 4). Residues of mancozeb (<0.05 ppm) and ETU (<0.01 ppm) were nondetectable (ND) in or on two samples. Apparent residues of mancozeb and ETU were <0.05(ND) and <0.01(ND) ppm, respectively in or on one untreated sample. Reported residue values were corrected for method recovery using 79% for mancozeb and 87% for ETU. Mancozeb analyses were conducted using a colorimetric method (Keppel) for mancozeb with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 83% from one sample fortified with mancozeb at 0.05 ppm, and 82% from one sample fortified with ETU at 0.01 ppm. Samples were stored frozen for 109 days prior to analysis for mancozeb and for 44 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. Storage stability data pertaining to frozen corn are available to support

this study (see "STORAGE STABILITY DATA" section). Mancozeb and ETU were stable for the time these samples were stored.

The Mancozeb Task Force (1988; MRID 41091701) submitted data from one test conducted in GA depicting residues of mancozeb and ETU in the wet milled product, starch and in the dry milled products, grits, flour, meal, crude oil, and refined oil. Field corn grain was harvested 41 days following the last of six foliar applications (using ground equipment) of the 80% WP formulation at 1.2 or 6 lb ai/A/application (1x or 5x the maximum single application rate allowed by PD 4; 0.6x or 3x the maximum seasonal application rate allowed by PD 4). Grain (two samples) bearing nondetectable (ND) residues of mancozeb (<0.05 ppm) and ETU (<0.01 ppm) was processed according to commercial procedures. Residues of mancozeb were <0.05(ND) ppm and residues of ETU were <0.01(ND)-0.01 ppm in or on four samples each of starch, grits (small, medium, and large), flour, meal, crude oil, and refined oil. Apparent residues of mancozeb and ETU were <0.05(ND) and <0.01(ND) ppm, respectively in or on one untreated sample of each processed product. Reported residue values were corrected for recovery using 92.2% for mancozeb and 88.2% for ETU. Mancozeb analyses were conducted using a colorimetric method (Keppel) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recovery from two samples of each processed product fortified with mancozeb at 5 and 10 ppm and of ETU at 0.2 and 2 ppm are presented in the table below. Samples were stored frozen for 208-215 days prior to analysis for mancozeb and for 209-210 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd.

Commodity	Percentage Recovery	
	Mancozeb	ETU
Corn grain	96.9	82.7, 81.2
Starch	86.6	110, 85.2
Small grits	92.2	97, 67.5
Medium grits	86.8, 89.5	84.9, 82.7
Large grits	92.2, 94.9	97, 76.2
Flour	89.5	84.9, 80.8
Meal	89.5, 92.1	129.7, 82.2
Crude oil	92	129.2, 76.3
Refined oil	86.6	84.9, 86.1

Geographic representation is inadequate since the test states of HI(<1%) and GA(1%) and neighboring states of NC(2%) and TN(1%) accounted for only ca. 5% of the 1988 field corn production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available field residue data indicate that residues of mancozeb will not exceed the established tolerance in or on field corn

grain harvested 54 days following the last of seven applications of the 80% WP formulation at 1.2 lb ai/A/application (1x the maximum single application rate allowed by PD 4; 0.7x the maximum seasonal application rate allowed by PD 4). Residues of ETU were <0.01(ND) ppm in or on these same samples. The available field residue data do not satisfy the requirements for reregistration because no data were submitted reflecting treatments made at 1x the maximum seasonal application rate or the minimum PHI allowed by PD 4.

The available processing data are inadequate to determine the potential for concentration of mancozeb and ETU residues because the commodities were processed from field corn bearing nondetectable residues of mancozeb and ETU. In addition, no data were submitted for the wet milled products, crude oil and refined oil, or for grain dust. Additional field and processing data are required.

Corn (sweet and popcorn)

Tolerance(s):

A tolerance of 0.5 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on popcorn grain and fresh corn (including sweet corn kernel plus cob with husks removed) [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered for multiple foliar applications to pop and sweet corn at 1.1-1.2 lb ai/A/application using ground or aerial equipment. Applications may be repeated as needed at 4-7 day intervals. A 7-day PHI has been established. Treated popcorn and sweet corn forage or fodder may not be grazed or fed to livestock. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for sweet corn and popcorn east of the Mississippi River and in AR and LA must be revised to specify a maximum application rate of 1.2 lb ai/A/application, a maximum of 15 applications or 18 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days. All labels bearing use directions for

sweet corn and popcorn west of the Mississippi River (except AR and LA) must be revised to specify a maximum application rate of 1.2 lb ai/A/application, a maximum of 5 applications or 6 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required field data depicting residues in or on sweet corn following multiple foliar applications of the WP and D formulations made using ground and aerial equipment in separate tests. The Guidance Document required the registrant(s) to propose label revisions establishing a maximum seasonal use rate or maximum number of applications per season. In addition, the Guidance Document required a processing study.

The earlier sweet corn residue data discussed in the Residue Chemistry Chapter were inadequate because inadequate geographic representation and lack of information on length and conditions of sample storage. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Sweet corn samples were stored 108 to 215 days before analysis. Residues of ETU were stable for six months of frozen storage in wheat and sweet corn. None of the available data match the PD 4 use pattern for use east of the Mississippi River. Field trial data from MN match the PD 4 use pattern west of the Mississippi River.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRID 41093201 and CBRS No. 9250; MRID 42155901) depicting residues of mancozeb and ETU in or on sweet corn kernels plus cobs (husks removed). The available data indicate that residues of mancozeb will not exceed the established tolerance of 0.5 ppm in or on sweet corn harvested 7 days following the last of seven applications of the 80% WP formulation at 1.2 and 6 lb ai/A/application (ca. 0.5x and 2x the maximum seasonal application rate allowed by PD 4) and following the last of fifteen applications at 1.2 lb ai/A/application (1x the maximum seasonal application rate allowed by PD 4). The submitted residue data do not satisfy the requirements for reregistration because geographic representation is inadequate. The required data for sweet corn will be translated to support the tolerance for mancozeb residues in or on popcorn. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, maximum of 15 applications or 18 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days for sweet corn and popcorn grown east of the Mississippi River, AR, and LA; and a maximum of 5 applications or 6 lb ai/A/season, a minimum

application interval of 4 days, and a minimum PHI of 7 days for sweet corn and popcorn grown west of the Mississippi River (except AR and LA).

- Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn harvested 7 days following the last of 15 foliar applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A applied at 4 day intervals. Tests must be conducted in FL(8%), NY(6%), and WI(19%) since these states accounted for most of the 1988 U.S. sweet corn production east of the Mississippi River (Vegetable, 1988 Summary, Ag. Statistics Board, NASS, USDA June 1989, p. 9 & 38). Samples must be analyzed within six months of sample collection.

- Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn harvested 7 days following the last of 5 foliar applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A applied at 4 day intervals. Tests must be conducted in OR(11%) and WA(14%), since these states, along with MN (17%), for which data are available, accounted for most of the 1988 U.S. sweet corn production west of the Mississippi River (Vegetable, 1988 Summary, Ag. Statistics Board, NASS, USDA June 1989, p. 9 & 38). Samples must be analyzed within four months of sample collection.

The Mancozeb Task Force also submitted processing data (MRID 41093201) depicting residues of mancozeb and ETU in cannery waste. The available processing data indicate that residues of mancozeb concentrate in cannery waste and that residues convert to ETU; however, the potential for concentration and the conversion factor could not be calculated since cannery waste was processed from sweet corn bearing nondetectable residues of mancozeb. The following additional data are required:

- Data depicting the potential for concentration of mancozeb residues of concern in cannery residue prepared from corn bearing measurable weathered residues. If residues concentrate/convert in this feed item, an appropriate feed additive tolerance must be proposed.

References (used):

MRID(s): 41093201. 42155901.

Discussion of the data:

The Mancozeb Task Force (1987; MRID 41093201) submitted data from two tests conducted in PA pertaining to residues of mancozeb and ETU in or on sweet corn (kernels plus cobs with husks removed;

K+CWHR) harvested 7 days following last of seven foliar applications (using ground equipment) of the 80% WP formulation at 1.2 or 6 lb ai/A/application (1x or 5x the maximum single application rate allowed by PD 4; 0.5x and 2.3x the maximum seasonal application rate allowed by PD 4). Residues of mancozeb were <0.05 ppm (nondetectable; ND) and residues of ETU were <0.01(ND) and 0.02 ppm in or on two samples of sweet corn (K+CWHR). Residues of mancozeb were 0.65 and 0.72 ppm in two samples of cannery waste processed from sweet corn treated at 1x the maximum single application rate allowed by PD 4 and were 5.3 and 5.4 ppm in two samples treated at 5x. Residues of ETU were 0.02-0.15 ppm in or on four samples of cannery waste. Apparent residues of mancozeb and ETU were <0.05(ND) and <0.01(ND) ppm, respectively in or on one untreated sample of corn (K+CWHR) and in two untreated cannery waste samples. Reported residue values were corrected for method recovery using 92% for mancozeb and for 99% for ETU. Mancozeb analyses were conducted using a colorimetric method (Keppel) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 63% from one sample of corn (K+CWHR) and 93.6 and 96% from two samples of cannery waste fortified with mancozeb at 0.05-5 ppm. Recoveries were 98% from one sample of corn (K+CWHR) and was 89 and 111% from two samples of cannery waste fortified with ETU at 0.01-0.05 ppm. Samples were stored for 41-343 days prior to analysis for mancozeb and for 49-347 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. Storage stability data pertaining to frozen corn reflecting these storage intervals and conditions are not available. Data indicate that residues of mancozeb are only stable for six months in frozen corn and wheat (see "STORAGE STABILITY DATA" section). In addition, no storage stability data pertaining to cannery waste are available. Residues of ETU in wheat declined to 72% of the original amount after one year of frozen storage.

Rohm and Haas Company (CBRS No. 9250; 1992; MRID 42155902) submitted data from one test conducted in OR depicting residues of mancozeb and ETU in or on sweet corn harvested seven days following the last of 15 foliar applications of the 80% WP formulation (using ground equipment) at 1.2 lb ai/A/application (1x the maximum seasonal application rate allowed by PD 4). Residues of mancozeb and ETU in or on samples of sweet corn cob plus kernels, ear plus husk, and husk are presented below.

Commodity	No. of samples	Residues (ppm) Mancozeb	ETU
cob plus kernels	2	<0.05(ND)	<0.05(ND)
ear plus husk	2	2.1, 2.46	0.11, 0.18
husk	2	4.7, 5.51	0.12, 0.21

Apparent residues of mancozeb and ETU were <0.05(ND) ppm and <0.01(ND) ppm, respectively in or on one untreated sample each of cob plus kernels (husk removed), ear plus husk, and husk. Reported residue values were corrected for method recovery using 96% for mancozeb; ETU residues were corrected for method recoveries using 77% for cob plus kernel and 96% for ear plus husk and husk. Mancozeb analyses were conducted using a colorimetric method (Keppel) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Samples were stored frozen (ca. -10 C) for 447-452 days prior to analysis. Storage stability data pertaining to frozen corn reflecting these storage intervals and conditions are not available. Data indicate that residues of mancozeb and ETU are only stable for six months in frozen corn and six months in frozen wheat (see "STORAGE STABILITY DATA" section). Residues of ETU in wheat declined to 60% of the original amount after two years of frozen storage. Method recoveries of mancozeb and ETU from one fortified sample each of cob plus kernel, ear plus husk, and husk are presented in the following table.

Sample	Fort.(ppm)	Percentage Recovery Mancozeb	ETU
cob plus kernels	0.05	95	--
cob plus kernels	0.01	--	77
ear plus husk	2	97	--
ear plus husk	0.02	--	94
husk	5	95	97

Geographic representation is inadequate since the test state of OR(11%) and MN(17%) accounted for only 28% of the 1988 sweet corn production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA June 1989, p. 9 & 38). The available data indicate that residues of mancozeb will not exceed the established tolerance of 0.5 ppm in or on sweet corn harvested 7 days following treatment at 1x the maximum seasonal application rate allowed by PD 4. The submitted field residue data do not satisfy the requirements for reregistration because geographic representation is inadequate.

Although analyses were not conducted within the time interval that residues of mancozeb and ETU are stable (six months), the data can be corrected for losses in frozen storage. The available processing data indicate that residues of mancozeb concentrate in cannery waste and that residues convert to ETU; however, the potential for concentration and the conversion factor could not be calculated since waste was processed from sweet corn bearing nondetectable residues of mancozeb. Additional field and processing data are required.

Wheat grain

Tolerance(s):

A tolerance of 5 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on wheat grain [40 CFR §180.176].

Food/feed additive tolerances have been established for the same residues at 20 ppm for wheat bran, 1 ppm for flour, and 20 ppm for milled feed fractions [40 CFR §185.6300 and §186.6300].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% F1C, and 70 and 75% DF formulations are registered for a maximum of three foliar applications per season to wheat at 1.2-1.6 lb ai/A/application using ground and aerial equipment. Treatments may be repeated at 7-10 day intervals. A 26-day PHI and pregrazing interval has been established. These formulations may also be used for seed treatments at 0.1-0.18 lb ai/100 lb seed. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for wheat must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 3 applications or 4.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 26 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data depicting residues in or on wheat grain following applications of the WP and D formulations using ground and aerial equipment in separate tests. The Mancozeb Guidance Document did not require processing studies for wheat based on data reviewed

Table 20. Summary of tentative residue characterization in goat tissues.

Fraction/ Component	Percent of the TRR		
	Liver	Kidney	Muscle
Identified mancozeb metabolites[a]	15.1-31.6	26.4-32.6	32.9-33.3
Natural components	(50.6-75.5)	(38.0-52.4)	(44.4-50.2)
Amino acids	32.2-59.1	26.7-31.2	27.3-32.2
Glycogen	1.6-3.3	3.7-8.0	0.1-0.5
Creatines	9.9-16.3	5.2-9.0	8.5-14.5
Lipids	1.7-4.9	4.2-8.5	3.7-7.9
Unidentified[b]	8.4-13.7	7.9-16.7	9.1-13.5
Losses	0.6-8.2	4.9-17.0	7.4-9.1

[a] Includes "unknown #1" present in the metabolite extracts and tentatively identified in urine as allantoin.
[b] Includes fractions unanalyzed.

Enforcement Analytical Method - Mancozeb and ETU

Muscle and liver tissues were analyzed for mancozeb, and ETU and milk was analyzed for ETU using currently available enforcement methods. Data depicting residues of mancozeb were analyzed using a gas chromatography method (modified by Keppel) with sulfur specific flame photometric detection (GC/FPD-S) with a limit of detection of 0.05 ppm and residues of ETU were analyzed using a GLC/FPD method (Haines and Adler). Residues of mancozeb were 0.21 ppm in liver and 0.3 ppm in muscle. Residues of ETU were 0.04 ppm in liver, 0.04 ppm in muscle, and 0.012 ppm in milk (day 7 sample). No data were submitted depicting mancozeb in milk, kidney, or fat and no data were submitted depicting ETU in kidney or fat. The registrant must submit data depicting the ability of the enforcement methods to detect mancozeb, ETU, and any other residues of concern in tissues of muscle, kidney, liver, fat, and milk.

Following reevaluation of the available data on ruminant metabolism, we conclude that the nature of the residue in ruminants is not adequately understood for the following reasons: (i) the only metabolite for which identity was confirmed was ETU, accounting for 5.2-28.6% of the TRR in milk, 0.5-1.3% of the TRR in liver, 1.9-2.6% in kidney, and 3.7-10.5% in muscle; (ii) metabolite identifications other than ETU are considered tentative because TLC resolution was poor and/or no confirmatory analyses were performed; (iii) evidence for the presence of radioactivity in natural products was inconclusive and the levels of ^{14}C-activity in these components was quite variable; and (iv) the maximum dosing level, equivalent to 36 ppm in the diet, may

not adequately represent the maximum theoretical dietary burden for dairy animals.

Metabolism in Laying Hens: Rohm and Haas Company submitted data (MRID 00160781) pertaining to the metabolism of mancozeb in white Leghorn laying hens. Twenty-five hens (5 groups; 5 hens/group) received oral capsular doses of [^{14}C]mancozeb for 7 consecutive days at a level equivalent to ca. 0, 3, 14, and 36 ppm in the diet. Eggs were collected daily, pooled by treatment groups, blended, and subsampled. Excreta from all dose groups were collected, pooled by treatment group, blended with water, and subsampled. The hens were sacrificed 24 hours after the final dose. Breast and thigh muscles, fat, liver, kidney, gizzard, and heart samples were collected, pooled by treatment groups, and homogenized. The total radioactivity in soluble samples, extracts, and unextractable residues in excreta, eggs and tissue samples were quantified either directly by liquid scintillation spectrometry (LSS) or following combustion (solid samples).

Total Radioactive Residues

The total radioactive residue (TRR) or ^{14}C-activity in soluble samples, extracts, and unextractable residues showed that 88.2% of the administered ^{14}C-activity was recovered in excreta, eggs, and tissues of the dosed hens (36 ppm dose group). The excreta, eggs, and tissues of hens dosed at 36 ppm contained 87.4%, 0.46% and 0.35%, respectively, of the recovered ^{14}C-activity. The highest concentrations of [^{14}C]mancozeb residues in the tissues of 1.92 and 1.98 ppm were found in liver and kidney, respectively. The level of ^{14}C-residues level in eggs from hens dosed at 36 ppm increased steadily from 0.025 ppm on the first day of sampling to a peak of 0.849 ppm on day 7 of sampling; residues in eggs from the 14 ppm dose group increased from 0.0088 ppm on day 1 to 0.261 ppm on day 7. Eggs from the low (3 ppm) dosed hens increased from 0.0197 ppm on day 2 to 0.0498 ppm on day 7; samples collected on days 3 and 6 bore residues below the limit of detection (<0.001 ppm). The summarized data are presented in Table 21. All analytical data were obtained from egg and tissue samples of the dose group hens administered 36 ppm of mancozeb.

Table 21. Percent distribution of recovered ^{14}C-activity in excreta, eggs, and tissues of hens dosed with [^{14}C]mancozeb at 3 to 36 ppm.

	Dosing level					
	3 ppm		14 ppm		36 ppm	
Tissue	%	ppm	%	ppm	%	ppm
Excreta	82.8	4.77	81.9	47.4	87.4	84.4
Whole Egg	0.193	0.05	0.376	0.260	0.463	0.849
Breast Muscle	0.0166	0.0105	0.0209	0.065	0.029	0.224
Thigh Muscle	0.0226	0.0142	0.0273	0.0846	0.0384	0.295
Kidney	0.0465	0.146	0.0515	0.747	0.0545	1.98
Liver	0.0888	0.097	0.134	0.692	0.138	1.92
Heart	0.0051	0.027	0.0055	0.146	0.006	0.429
Gizzard	0.0448	0.073	0.0836	0.662	0.0761	1.46
Fat	0.0016	0.008	0.005	0.064	0.005	0.237
Total	83.3		82.6		88.2	

Extraction

Excreta, egg, and tissue samples were solvent extracted. Each extraction consisted of solvent addition, homogenization, centrifugation, separation, and radioanalysis. Unextractable residues were combusted and radioassayed. Portions of the unextractable residues from egg and tissue samples were digested in 6N HCl.

Kidney samples were extracted with methanol:chloroform:water (11:55:5, v:v:v), methanol, water, and hexane. About 27% of the total ^{14}C-activity in kidney samples was extractable. A portion of the combined methanol:chloroform:water extracts was radioassayed and the remainder partitioned with chloroform:water (32:5, v:v). The aqueous methanol layer was removed from the semi-solid methanol:chloroform interface. Most of the ^{14}C-activity partitioned into the aqueous methanol layer. Chloroform-soluble residues were re-extracted with 60% methanol and the aqueous methanol extracts were pooled and filtered to remove traces of suspended solids. The aqueous methanol layer was fractionated into neutral, basic, and acidic fractions. The neutral and basic fractions were analyzed using TLC on silica gel plates developed with ethyl acetate:2-propanol:water (65:25:10 or 3:1:1, v:v:v; solvent system A) and 2-propanol:ammonium hydroxide (4:1, v:v; solvent system B). A major unknown was isolated and re-chromatographed using TLC on silica gel plates developed with chloroform:ethyl acetate:methanol:2N ammonium hydroxide (3:5:3:1, v:v:v:v) and ethyl acetate:water:acetone (3:1:1, v:v:v). The unknown metabolite did not co-chromatograph with any known mancozeb metabolite. Metabolites were visualized by

radioautography, UV-light, fluorescence, and/or the following colorimetric spray reagents: (i) FN Reagent (for EBIS, ETU, hydantoin, Jaffe's Base, and IMD); (ii) Erhlich's Reagent (for EU); and (iii) Fluorescamine (for N-acetylethylene-diamine, EDA, and glycine).

The sample of whole egg was extracted similarly but without methanol extraction and only chloroform was added to the combined methanol:chloroform:water extracts.

Thigh muscle samples were extracted with hexane, methanol, and water. The combined aqueous methanol extracts were partitioned with chloroform. The aqueous layer was removed, filtered, and separated into neutral, basic, and acidic fractions by ion exchange chromatography. The neutral fraction was analyzed using TLC on silica gel plates developed 2-propanol:ammonium hydroxide (4:1, v:v). Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS. About 65% of the ^{14}C-activity in thigh muscle tissue was solvent extractable.

Breast muscle samples were extracted with methanol:chloroform:water (11:5:5, v:v:v), chloroform:methanol (2:1, v:v), methanol, and water. The methanol and chloroform:water extracts were combined and partitioned with chloroform. The aqueous layer was removed, filtered, and fractionated by ion exchange chromatography. The neutral fraction was analyzed using TLC on silica gel plates developed with solvent systems A and B as previously described. Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS.

Liver samples were sequentially extracted with methanol:chloroform:water (11:5:5, v:v:v), methanol:chloroform (11:55,v:v), chloroform:methanol (2:1, v:v), methanol, and water. The methanol:chloroform:water extracts were combined. A portion of the combined extracts was radioassayed and the remainder was combined with chloroform:water (7:1, v:v). The aqueous methanol layer was decanted and allowed to separate into water and methanol fractions. The fractions were dried, suspended with water and methanol, respectively, and analyzed using TLC developed with solvent systems A and B. Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS.

The unextractable residues from eggs and tissues were digested in 6N hydrochloric acid at 110 C for 18-24 hours and the hydrolysates were filtered. The filtrates were concentrated by evaporation and radioassayed. The acid hydrolysates were fractionated by ion exchange chromatography; basic and neutral fractions (breast, thigh, and kidney eluates), and basic

fractions (liver eluates) were analyzed using TLC as earlier described. Metabolites were visualized by radioautography, UV-light, fluorescence, and the colorimetric spray reagents previously described, then quantified by LSS. About 83-92% of the total ^{14}C-activity in solvent unextractable egg and tissues residues was hydrolyzed by protease and/or acid. Approximately 3-7% of the total activities in eggs and tissues were not hydrolyzable.

Protease-digested residues in liver and eggs were reacted with dansyl chloride. The mixtures were extracted with toluene to remove didansyl ethylenedithiourea and didansyl N-actyl ethylenedithiourea leaving dansylated amino acids in the aqueous phases. The toluene and aqueous phases were analyzed using TLC (details not provided).

Characterization/Identification

Fractionated and unfractionated solvent extracts and acid hydrolysates of the ^{14}C-residues in egg and tissues were analyzed by co-migration with known unlabeled mancozeb degradation products on TLC plates. The metabolites in solvent extracts and acid hydrolysates were separated and tentatively identified using TLC on silica gel plates developed with the solvent systems described above (see "Extraction" section) for each tissue. The ^{14}C-residues in egg and tissue extracts were tentatively identified as ethylenebisthiocarbamate (EBIS), ethylenethiourea (ETU), hydantoin (HYD), 2-imidazoline (IMID), ethylenediamine (EDA), N-acetyl ethylenediamine (N-AcEDA), ethyleneurea (EU), and Jaffe's Base (JB). EBDC residues and metabolites in eggs and tissues also were analyzed using GC on a Tenax GC column and quantified using a flame photometric detector (FPD) in the sulfur specific mode. Residues of EBDC were decomposed to CS_2 gas following acid hydrolysis of tissue and egg samples; the CS_2 gas was trapped in ethanol on dry ice prior to analysis. Confirmatory analysis of EBDC residues was conducted by analyzing an aliquot of the CS_2-containing ethanol using GC/MS under operating conditions identical to the EBDC GC/FPD method. The ionization source for MS was unspecified. ETU residues in eggs and tissues were analyzed by GC/FPD on a 10% Carbowax 20M/2% KOH column. Prior to GC/FPD analysis, ETU residues were converted to their *S*-butyl derivatives with bromobutane in the presence of dimethylformamide and sodium borohydride. Confirmatory analysis of ETU residues was conducted by analyzing an aliquot of the derivatized residues extracted from eggs and tissues by GC/MS under operating conditions identical to the ETU GC/FPD method.

Summaries of the patterns of residue extraction from eggs and tissues and tentative identifications mancozeb metabolites are presented in Tables 22-27.

Table 22. Distribution of radioactivity in eggs from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 0.849 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
First extraction:		
Methanol/water	(40.2%; analyzed using TLC)	
EBIS	0.12	0.001
ETU	6.8	0.058
EU	20.3	0.172
EDA/GLY	1.5	0.013
NAcEDA	3.1	0.026
Origin/unknown	8.3	0.070
Chloroform	5.0	
Methanol	5.0	
Water	4.4	
Hexane	1.1	
Unextracted	44.2	
Second extraction:		
Methanol/water	(34.1%; analyzed using TLC)	
ETU	0.72	0.006
EU	21.2	0.180
JB	0.68	0.006
NAcEDA	0.72	0.006
HYD	1.64	0.014
EDA/GLY	1.57	0.013
Origin	4.71	0.040
Chloroform	(21.2%; analyzed using TLC)	
EBIS	0.19	0.002
ETU	1.46	0.012
EU	8.06	0.068
NAcEDA	0.23	0.002
HYD	0.42	0.004
EDA/GLY	1.8	0.015
Origin	2.5	0.021
Water	3.4	
Hexane	4.3	
Unextracted	(33.4)	
Acid hydrolyzed	33.0	
ETU/JB	0.3	0.003
EU	0.7	0.006
HYD	0.87	0.007
IMID	1.97	0.017
EDA/GLY	8.98	0.076
Origin	8.15	
Dansylated protease hydrolysate		
Dansyl gly	2.1	0.018
Dansyl amino acids	6.1	0.052

Table 23. Distribution of radioactivity in fractions of thigh muscle from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 0.295 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
First extraction		
Methanol/Aqueous	(48.1%)	
Neutral	(31.0%; analyzed using TLC)	
EU	13.9	0.04
N-AcEDA	1.0	0.003
EDA/GLY	2.8	0.008
HYD	0.7	0.002
IMID	1.9	0.006
Origin/unknown	10.8	
Basic	14.4	
Acidic	4.2	
Chloroform (lipid)	2.9	
Hexane (lipid)	0.8	
Water	5.2	
Unextracted	(39.1)	
Acid hydrolyzed	30.9	
Second extraction		
Methanol	50.5	
Water	4.4	
Hexane	0.5	
Unextracted	(44.6)	
Protease hydrolyzed	(37.2)	
Basic fraction	(31.7; analyzed using TLC)	
EU	1.5	0.004
N-AcEDA	3.3	0.015
EDA/GLY	9.9	0.029
HYD	4.2	0.012
Origin/unknown	5.4	
Neutral fraction	3.6	
Unhydrolyzed	7.4	

Table 24. Distribution of radioactivity in fractions of breast muscle from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 0.224 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
First extraction		
Methanol/ aqueous	(55.7%)	
Neutral	(36.4%; analyzed using TLC)	
EU	35.9	0.08
Basic	15.0	
Acidic	1.0	
Chloroform (lipid)	5.1	
Water	1.5	
Chloroform/methanol	1.5	
Unextracted	(35.3%)	
Acid solubilized	(36.0)	
Basic	26.9	
acidic	0.8	
neutral	0.4	
Acid insoluble	0.0	
Second extraction		
Methanol:chloroform:water	57.6	
Water	1.2	
Unextracted	(41.1%)	
Protease digested	(34.4)	
Basic	(28.6%; analyzed using TLC)	
EU	1.1	0.002
EDA/GLY	9.87	0.022
Origin/unknown	18.36	
Other	2.8	
Undigested	6.7	
Neutral/acid	1.2	

Due to dissimilarities in the first and second extractions, estimates of identified bound and free metabolites and uncharacterized fractions were not made. EU (35.9% of the TRR), was the only free metabolite identified in the first extraction; based on data from the second extraction, bound EU could account for an additional 1% of the TRR and bound EDA and/or GLY, ca.10%. Therefore, a minimum of 53% of the TRR in breast muscle was not characterized.

Table 25. Distribution of radioactivity in fractions of kidney from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 1.98 ppm).

Fraction/ metabolite	Total radioactive residues (%)	Mancozeb equivalents (ppm)
Aqueous	(21.1)	
Neutral	(5.0%; analyzed using TLC)	
EU	3.55	0.071
Origin/unknown	1.6	
Basic	(10.8%; analyzed using TLC)	
EDA/GLY	3.74	0.074
EU	0.238	0.005
EBIS	1.02	0.020
ETU/JB	0.183	0.004
Origin/unknown	5.6	
Acidic	4.7	
Chloroform (lipid)	3.7	
Water	1.4	
Unextracted	(73.0)	
Acid hydrolyzed	(70.0%; analyzed using TLC)	
EDA/GLY	25.76	0.510
ETU	0.77	0.015
EU	1.68	0.033
NAcEDA	6.02	0.119
HYD	6.9	0.137
EBIS	0.42	0.008
Origin/unknown	20.37	
Protease hydrolyzed	(67.5)	

Table 26. Distribution of radioactivity in fractions of liver from hens dosed with [^{14}C]mancozeb at 36 ppm (TRR = 1.92 ppm).

Fraction/ metabolite	Percent of TRR	Mancozeb equivalents (ppm)
First extraction		
Methanol:water	(33.6%; analyzed using TLC)	
ETU	0.3	0.006
EU	4.5	0.086
NAcEDA	0.4	0.008
HYD/IMID	2.2	0.042
GLY/EDA	4.1	0.079
Origin/unknown	25.7	
Chloroform	4.1	
Water	8.8	
Chloroform:Methanol	1.0	
Unextracted	(49.2)	
Acid hydrolyzed	(44.9)	
Basic	41.2	
Neutral	0.6	
Acidic	0.8	
Protease digested	(42.5)	
Basic	(34.8% analyzed using TLC)	
EBIS	0.3	0.007
ETU/JB	0.4	0.008
EU	0.5	0.010
NAcEDA	0.6	0.011
HYD	1.5	0.030
IMID	2.5	0.049
EDA/GLY	9.8	1.89
Origin/unknown	17.4	
Neutral	0.3	
Acidic	0.5	
Second extraction		
Extracted (unspecified)	42.3	
Unextracted	57.7	
Protease digested	(51.5; dansylated and analyzed using TLC)	
Dansyl-EDA	3.2	0.062
Dansyl-NAcEDA	0.9	0.017

Table 27. Summary of residues in hen eggs and tissues.

Component	Percentage of TRR			
	Egg	Muscle	Kidney	Liver
Identified degradates	51.28	40.2	50.28	27.1
Unidentified	15.36	16.4	27.57	43.0
Unanalyzed extracted	7.7	23.1	9.8	14.7
Unhydrolyzed	5.5	7.4	3.0	6.7
Unexplained	22.8	12.1	9.35	8.5

The registrant additionally presented data concerning residues of mancozeb and ETU analyzed using GC methods; the reported residues were corrected for method recovery. For comparison, ETU residues estimated using TLC on silica gel plates developed with ethyl acetate:2-propanol:water (65:25:10, v:v:v) and 2-propanol:ammonium hydroxide (4:1, v:v) are presented below in Table 28. The metabolites were visualized and quantified using the previously described methods.

Table 28. Mancozeb (CS_2-containing residues) and ETU in excreta, eggs, and tissues from hens dosed at 36 ppm.

Sample	Mancozeb (ppm)	ETU (ppm)	ETU (ppm)
Excreta	23.1	3.71	ND[a]
Whole Egg	0.012	0.057	0.06
Breast	0.037	<0.007	ND
Thigh	0.069	<0.007	ND
Liver	0.165	0.003	0.004
Gizzard	0.15	0.007	ND
Kidney	0.14	<0.007	<0.007
Fat	0.13	0.01	ND

[a] ND indicates no detectable residue on the TLC.

After reexamining the poultry metabolism data, we conclude that the requirement for additional data remains outstanding. Only ca. 30-50% of the TRR in eggs and tissues was characterized, and most of those identifications are considered tentative due to poor separation of metabolites on TLC or the failure to perform confirmatory analyses. In eggs, the only metabolites with verified identities were ETU (up to 7% of the TRR) and glycine (maximum of 10%; uncertain due to the co-migration of EDA with underivatized glycine on TLC). In liver, the presence of ETU was confirmed (<1% of the TRR), as were NAcEDA (1%) and EDA (percentage undetermined due to co-migration of glycine with EDA). We do not consider unanalyzed fractions from ion exchange

chromatography or radioactivity at the origin of TLC plates to be sufficiently characterized. With regard to the lack of data on metabolites in fat, we maintain that these data requirements remain outstanding.

RESIDUE ANALYTICAL METHODS

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required multiresidue testing for mancozeb and ETU. The Mancozeb Residue Chemistry Chapter, dated 9/86, required the registrant to develop methodology specific for mancozeb and suitable for enforcement purposes.

In response to the Guidance Document, the Mancozeb Task Force submitted multiresidue test data (1988: MRID 40764601); these data have been forwarded by EPA to the Food and Drug Administration (FDA) for review. According to the Pestrak data base (10/13/89; PAM Vol. I, Appendix), mancozeb is not likely to be recovered by FDA Multiresidue Protocols A-E; special surveys have occurred with other methods. ETU is variably recovered by Protocol A using special gas chromatography (GC) or high performance liquid chromatography (HPLC) methods; special surveys have also been conducted on ETU with other methods.

The analytical methods currently in use today for mancozeb determination are all modifications of the basic dithiocarbamate method described by Pease (JAOAC 40:1113-1118). These methods are based on the liberation of carbon disulfide from the EBDC moiety by acid digestion in the presence of stannous chloride, followed by determination of the carbon disulfide produced using colorimetry or GC. These methods are not specific for the individual EBDCs analyzed and will not differentiate other degradates such as EBIS that may be converted to carbon disulfide. Plant residue data reviewed in this document were analyzed using the Keppel method (JAOAC, 54:528-532). This method is listed as method III in PAM Vol. II and currently is used by FDA for enforcement purposes. Mancozeb residues are decomposed to carbon disulfide by refluxing with boiling dilute acid. Evolved carbon disulfide is carried through a trap to remove hydrogen sulfide and other volatile interferences. In a second trap, the carbon disulfide is reacted to form a yellow complex, cupric salt of N, N-bis(2-hydroxyethyl)dithiocarbamic acid, which is measured colorimetrically at 435 nm. A standard curve is prepared by carrying several amounts of analytical standards of mancozeb through the method and is constructed using linear regression.

A description of GC methods for the determination of EBDCs in crops and processed products (MTF-89-AM-001, G. Westberg, Morse Laboratories, 6/7/89), meat (ETU-89-AM-002, G. Westberg, Morse Laboratories, 8/25/89), and milk (ETU-89-AM-003, G. Westberg, Morse Laboratories, 8/25/89) were submitted (MRID 41343101) and reviewed by the Agency (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) for the EBDC/ETU monitoring study. By these methods, EBDCs are decomposed by reaction with HCl/stannous chloride and EDTA to carbon disulfide. Evolved carbon disulfide is analyzed using GC using equipped with an Alltech 223 packed column and a flame photometric detector (FPD) in the sulfur mode.

Analytical methodology for ETU is based on the original method published by Onley and Yip (JAOAC 54:165-169). ETU is extracted with aqueous methanol, cleaned up by column chromatography and then analyzed by GC as the S-butyl derivative, following reaction of ETU with 1-bromobutane. Derivatized ETU may also be quantitated using GC with a sulfur specific detector; alternatively, underivatized ETU may be determined using HPLC with a reverse phase C-18 column (Morse Laboratories 7/27/89). Plant residue data reviewed in this document were analyzed using HPLC and gas liquid chromatography (GLC) method. By the GLC method, the crop is extracted with methanol, the methanol extract (containing ETU) is concentrated by rotary evaporation, and cleaned up on an alumina column. The concentrated extract is derivatized with 1-bromobutane to form butyl-ETU. The butyl-ETU is extracted with chloroform, solvent exchanged into toluene, and analyzed using GLC with a 10% carbowax column with flame photometric detection (sulfur mode). Quantitation is by external standard using ETU standards in toluene. A standard curve is prepared over the concentration range of interest, using peak height measurements.

Methodologies for ETU determination in crops (MTF-88AM-004, E. Rodgers, K. Tufts, G. Westberg, Morse Laboratories, 7/10/87, revised 7/27/89), meat (ETU-89AM-004, E. Rogers, K. Tufts, S. Normington, and G. Westberg, Morse Laboratories, draft 9/13/89), and milk (ETU-89AM-005, E. Rodgers, K. Tufts, S. Normington, and G. Westberg, Morse Laboratories, draft 9/13/89) were submitted (MRID 41343101) and reviewed by the Agency (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) for the EBDC/ETU monitoring study. These methods involve extraction of ETU using methanol or ethanol, filtration through celite, concentration, and clean-up on a alumina column. The concentrated extract is analyzed using HPLC with a reverse phase C-18 column, 5% methanol in water as the mobile phase, and UV or electrochemical detection.

At the present time, analytical methods converting all EBDCs and some metabolites to carbon disulfide will be considered adequate for enforcement, along with a specific method for ETU. If any

additional residues on concern are found in the metabolism studies currently in progress, additional methodology may be required. The following data requirement remains outstanding:

- If the requested data regarding the nature of the residue in plants and animals reveal additional metabolites of toxicological concern, additional analytical methods for data collection and enforcement may be required.

References (used):

MRID(s): 40764601. 41343101.

Discussion of the data:

The Mancozeb/ETU Task Force submitted a preliminary report (MRID 41343101) pertaining to the method validation which has been reviewed by the Agency (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) for the EBDC/ETU monitoring study. EBDC (mancozeb) and ETU residues in crops, processed commodities, milk, and meat were analyzed using Morse Laboratory methods. Descriptions of these methods, summarized by CBRS (EPA Memoranda CBRS Nos. 6357, 6358, and 6359, S. Hummel, dated 7/16/90) are reiterated here for clarity.

EBDCs in crop and processed commodities (MTF-89-AM-001, G. Westberg, Morse Laboratories, 6/7/89), meat (ETU-89-AM-002, G. Westberg, Morse Laboratories, 8/25/89), and milk (ETU-89-AM-003, G. Westberg, Morse Laboratories, 8/25/89): EBDC residues in frozen, ground crop and processed commodity samples or meat samples or quick thawed milk samples are decomposed by reaction with HCl/stannous chloride in a sealed reaction flask in a boiling water bath. EDTA solution is added to the flask before reaction. Evolved carbon disulfide in the headspace (airspace) is analyzed using headspace GC with an Alltech 223 packed column and a flame photometric detector (FPD) in the sulfur mode after the column is preconditioned with CS_2. Standards and fortified samples are prepared and analyzed in the same manner. The limit of detection was reported to be 0.02 ppm. Quantitation is by external standard and a calibration curve on log/log paper.

ETU in crops (MTF-88AM-004, E. Rodgers, K. Tufts, G. Westberg, Morse Laboratories, 7/10/87, revised 7/27/89): ETU is extracted from the chopped crop or meat samples, or milk samples with water:ethanol (crops and milk) or water:methanol (meat), pH adjusted to 11-12 with NH_4OH. The extract is pH adjusted to 7-9, filtered through celite, concentrated by rotary evaporation with a decanol keeper, and cleaned up on a alumina column. The ETU is eluted with ethanol:chloroform (4:96 or 6:94, v:v). The eluate is concentrated by rotary evaporation. The concentrated extract is analyzed using HPLC with a reverse phase C-18 column, 5% methanol in water as the mobile phase, and detection by UV at 233

nm or by electrochemical detection. Quantitation is by external standard using a calibration curve. The limit of detection of the method was reported to be 0.01 ppm for crops and was not reported for meat or milk. Although not documented in the method, electrochemical detection was used for tomato paste.

The recoveries of mancozeb and ETU from fortified crop, milk, and meat samples are presented in Table 35.

Table 35. Recovery of mancozeb and ETU from fortified crop, milk, and meat samples.

Matrix	Laboratory	Fortification level (ppm)	Recovery (%)
Mancozeb:			
Apple	Craven[a]	0.02-2.0	96-102
Banana	Craven[a]	0.02-2.0	91-109
Celery	McKenzie	0.02-2.0	90-94
Snap beans	McKenzie	0.02-2.0	88-97
Corn	EN-CAS	0.02-2.0	Not complete
Potato	Morse	0.02-2.0	89-92
Tomato	Morse	0.005-0.02	98-115
Milk	Morse	0.002-0.02	108-110
Meat	Morse	0.002-0.02	82-103
ETU:			
Apple	Craven[a]	0.01-1.0	78-87
Banana	Craven[a]	0.01-1.0	88-106
Celery	McKenzie	0.01-1.0	82-100
Snap beans	McKenzie	0.01-1.0	79-87
Dry beans	EN-CAS	0.01-1.0	75-84
Corn	EN-CAS	0.01-1.0	81-91
Potato	Morse	0.002-1.0	79-102
Tomato	Morse	0.002-0.01	79-93
Tomato paste	Morse	0.002-0.01	76-84
Milk	Morse	0.001-0.01	72-88
Meat	Morse	0.001-0.01	67-74

[a] Data from Craven Laboratories are not used in this Update document to support the requirements for reregistration.

For purposes of the EBDC/ETU monitoring study, CBRS concluded the following: (i) analytical methods must be validated in each matrix (commodity) for which data are to be submitted; (ii) the recovery values reported for the matrices tested (apples, bananas, celery, snap beans, potatoes, tomatoes, milk, and meat) were adequate; however, recovery data are still needed for each commodity study submitted and recovery must be determined with each set of samples analyzed; (iii) chromatograms submitted for EBDC analyses indicate interferences in tomatoes, meat, and milk;

and (iv) the residue levels must be measured and reported at the lowest limit of detection possible.

STORAGE STABILITY DATA

Conclusions:

The Mancozeb Guidance Document, dated 4/87, concluded that the available storage stability data are adequate to demonstrate that mancozeb is stable in or on frozen apple and tomato samples for up to 12 months, and ETU is stable for up to 6 months. The Guidance Document required storage stability studies on both weathered and fortified frozen samples from representative crops from each crop grouping and fortified storage stability data for processing studies. In addition, the Guidance Document required storage stability data depicting the decline in residues of mancozeb and percentage decline or increase of ETU for animal commodities.

In response to the Guidance Document, the Mancozeb Task Force submitted storage stability data (MRID 41070001) for selected crops which were reviewed by CBRS (EPA Memorandum CBRS No. 5280, S. Hummel, dated 8/17/89). CBRS concluded that under the conditions used by the laboratory (Enviro-Bio-Tech Ltd.) performing the study, mancozeb is stable in or on apples, tomatoes, and wheat for six months. ETU is stable in tomatoes and wheat for six months, but only stable for one month in frozen apples. CBRS stated that storage stability data by Enviro-Bio-Tech Ltd.

In an Agency memorandum (EPA Memoranda CBRS Nos. 4656, 4707, and 4995, S. Hummel, dated 10/25/90), it was concluded that although no additional storage stability data are required to support the previously reviewed residue field trials, storage stability data are required for additional residue field trial studies submitted.

The ETU Task Force submitted storage stability data (MRID 41643601) with the fourth quarter and final report for the EBDC/ETU monitoring study as required by the EBDC Special Review Data-Call-In Notice of 3/10/89. These data were reviewed by S. Hummel (CB No. 7155, and HED No. 0-2032, dated 12/4/90) who concluded that under the storage conditions used in the market basket survey, these data indicate that mancozeb (fortified samples) was stable for only 1 month in potatoes, for up to 4 months in dry beans, frozen corn, lettuce, and for up to 6 months in tomatoes, meat, and milk. It was further concluded that ETU was stable for three months or longer in coarsely ground fortified samples of dry beans, corn, meat, milk, and tomatoes; 2 months in lettuce; and 0.5 months in potatoes. In finely ground fortified samples, ETU was stable for 12 days in dry beans,

frozen corn, lettuce, tomato, and meat; ETU was stable for only 5 days in potatoes. No weathered storage stability data are available on representative crops where mancozeb uses are allowed.

Rohm and Haas Company submitted data (1991; MRID 41976101; CBRS No. 8513) performed by Enviro-Bio-Tech Ltd. pertaining to the storage stability of mancozeb and ETU in or on whole apples that had been sprayed with mancozeb or ETU. These data indicate that residues of mancozeb are stable in or on fortified whole apples samples for up to 549 days of frozen storage. The data also indicate that residues of ETU are stable for up to 31 days in or on whole apples treated with ETU. Frozen storage stability of ETU residues in or on whole apples treated with mancozeb could not be determined because the ETU recovery percentages were quite variable. Recoveries of ETU from mancozeb-fortified samples ranged from 63% (day 184) to 180% (day 31); although recoveries of ETU greater than 100% indicate conversion of mancozeb to ETU, the calculated conversion factors were rather negligible (0.1-2%).

The samples from field residue and processing data reviewed in this Update document were analyzed by Enviro-Bio-Tech Ltd., with the exception of processed potato samples (MRID 41091601) which were analyzed by National Food Laboratory (Washington, D.C.). In these studies, mancozeb analyses were conducted using a colorimetric method (Keppel) and ETU analyses were conducted using a GLC method (Onley). A summary of the duration of frozen storage prior to analysis for each crop and processed products reviewed in this Update is presented in Table 36. The results of storage stability studies of mancozeb and ETU in various raw agricultural commodities under frozen conditions are presented in Tables 37 through 42.

The field residue data submitted for tomatoes, cranberries, field corn grain, and seed treatment of wheat grain are supported by acceptable storage stability data.

The field residue data submitted for potatoes, apples, sweet corn, and wheat grain (seed treatment) are not supported by storage stability data because samples were stored at intervals longer than when either mancozeb or ETU are stable under the same conditions.

No storage stability data are available for asparagus, bananas, cucumbers, field corn fodder, grapes, onions, papayas, peanuts (nutmeats, vines, hay, and hulls), pears, potatoes (processed products), sugar beets and sugar beet tops, sweet corn (cannery waste), wheat straw, and seed treatments (stems and leaves). No data have been submitted concerning the storage stability of mancozeb residues of concern in animal tissues. The following data requirements remain outstanding:

- To support the field residue and processing data required in this Update document, storage stability studies must be concurrently conducted (in the same laboratory, under the same conditions, and for the same duration) with the field residue and processing studies. If samples from the field residue and processing studies are analyzed within two weeks of collection, and all fresh samples are frozen within a few hours of collection, and all analyses are completed on the same day on which they were begun (from grinding the sample through the determinative step), then the requirement for concurrent storage stability data may be waived. Protocols for these studies must be submitted to and approved by the Agency prior to initiating the studies.

- If cattle and poultry feeding studies are required, then fortified storage stability studies will be required on all animal commodities (i.e. tissues, milk, and eggs) for which residue data are submitted to the Agency. Analyses must be conducted over a time period that includes the time interval that each commodity is held in frozen storage prior to residue analyses.

- The nature of the residue in plants and animals is not adequately understood. If the requested data on plant and animal metabolism indicate the presence of additional metabolites of toxicological concern, data depicting stability of these residues during storage will be required.

Table 36. Summary of the duration of storage (frozen) for commodities reviewed in this document.

MRID	Commodity	Days of Storage Mancozeb	Days of Storage ETU
41092007	apples	34-427	39-432
41976101	apples	0-549	0-549
40869701	asparagus	292	292
40869702	asparagus	459	494
40913303	bananas	196	199
40913304	bananas	168	63
40869705	field corn	109	44
41091701	processed field corn	208-215	209-210
41093201	sweet corn	41-343	49-347
40869706	cranberry	31	33
41092006	cucumbers	389-413	396-418
40869707	cucumbers	553	496
41092001	grapes	97-114	131-148
41092002	grapes	52-57	64
41483801	processed grapes	231	235-267
40869708	onions	336-350	346-360
41092003	onions	37	44
40869709	papaya	40	48
40869710	papaya	63	71
40869711	peanuts	17	17
41092004	peanuts	408	412
40913306	pears	108-122	383-397
40913301	potatoes	307-324	309-326
41091601	potatoes	13	15
41091601	processed potatoes	152-244	152-244
40869712	sugar beets	286-314	286-322
41091801	seed treatment	14-82	25-212
40768001	processed tomatoes	7-33	14-40
40869713	tomatoes	314-324	319-329
40869714	tomatoes	101-112	97-117
41092005	wheat	483	478
40869716	wheat	57-78	65-86
40869715	wheat	70	74

References (used):

MRID(s): 41070001. 41643601. 41976101.

Discussion of the data:

Rohm and Haas Company (1989; MRID 41070001, Report No. 34C-88-56) submitted data from a study performed by Enviro-Bio-Tech Ltd. pertaining to the storage stability of mancozeb and ETU in or on apples, tomatoes, and wheat. Commodities from untreated residue studies were analyzed for mancozeb and ETU to confirm the initial absence of these compounds. The untreated samples were then fortified with mancozeb at 1 ppm or with ETU at 0.1 ppm. The fortified samples were immediately (day 0) analyzed and stored at -20 C for 30, 180, 365, and 730 days. The commodities were analyzed for mancozeb using a colorimetric method (Pease as modified by Keppel; JAOAC, 54:528-532) and for ETU using an HPLC method (modified Onley method; JAOAC, 60:1105-1110). The limit of detection was 0.5 ppm for mancozeb and 0.02 ppm for ETU. The stability of mancozeb and ETU between 0 and 24 months is presented in Table 37; the method recovery for each commodity is presented in Table 38.

Table 37. Percentage recovery of residues from apples, tomatoes, and wheat fortified with mancozeb at 1 ppm and ETU at 0.1 ppm and stored frozen (-20 C) for 0-24 months.

	Percentage Recovery[a]									
	Mancozeb (months)					ETU (months)				
Commodity	0	1	6	12	24	0	1	6	12	24
Apples	100	103	101	75	76	95	103	64	46	50
Tomatoes	103	101	98	71	76	96	101	82	76	58
Wheat	98	100	102	81	76	92	102	87	72	60

[a] Reported values for mancozeb were corrected for average method recovery using 97% for apples, 97% for tomatoes, and 99% for wheat. Reported values for ETU were also corrected using 94% for apples, 95% for tomatoes, and 94% for wheat.

Table 38. Method recovery for mancozeb and ETU from apples, tomatoes, and wheat.

	Method Recovery (%)									
	Mancozeb (months)					ETU (months)				
Commodity	0	1	6	12	24	0	1	6	12	24
Apples	95	97	97	98	100	87	90	94	96	101
Tomatoes	95	97	97	97	98	83	94	98	100	102
Wheat	94	98	100	101	102	89	92	94	94	101

The data presented on previous tables indicate that mancozeb and ETU residues decline in apples, tomatoes, and wheat under the tested conditions. Decline of mancozeb in these commodities for the tested intervals appears to be limited. However, ETU residues declined rapidly in apples after 1 month of frozen storage and in tomatoes and wheat after 12 months of storage. Additional storage stability data are required to support field residue and processed products data submitted for tolerance assessment.

The ETU Task Force (MRID 41643601) submitted storage stability data with the fourth quarter and final report for the EBDC/ETU monitoring study as required by the EBDC Special Review Data-Call In-Notice of 3/10/89. An updated report (MRID 41831401) was submitted with additional storage intervals for dry beans and corn. These data were reviewed by the Agency (CB No. 7155, and HED No. 0-2032, S. Hummel, dated 12/4/90 and CB No. 7901, HED No. 1-1089, S. Hummel, dated 5/4/92) and are reproduced in Tables 39 and 40 for information purposes.

Table 39. Storage stability of mancozeb in finely ground frozen raw agricultural commodities from the EBDC/ETU Market Basket Survey.

Commodity[a]	Percent of original amount at intervals (months)						
	0	0.5	1	2	3	4	6
Beans, dry	84	123	102	117	108	98	120
Corn, frozen	85	113	101	96	90	86	103
Lettuce	97	96	91	91	87	95	NA
Potato	100	84	77	59	NA	NA	NA
Tomato	96	90	91	NA	92	NA	100
Meat	100	98	92	NA	112	NA	112
Milk	102	109	89	NA	98	NA	79

[a] Crop samples were fortified at 2 ppm; meat and milk samples were fortified at 0.5 ppm.

Table 40. Storage stability of coarsely ground and finely ground commodities fortified with ETU.

Commodity[a]	Coarsely ground (months)						Finely ground (days)		
	0	0.5	1	3	4	6	0	5	12
Beans, dry	91	96	97	81	85	94	79	95	95
Corn, frozen	83	97	102	95	95	89	85	103	101
Lettuce	113	94	107	55	NA	NA[b]	97	103	117
Potato	99	84	64	47	NA	NA	92	72	76
Tomato	100	104	105	93	NA	89	97	103	97
Meat	102	108	106	95	NA	110	101	112	108
Milk	94	97	106	95	NA	96	NA	NA	NA

[a] Crop samples were fortified at 0.5 ppm; meat and milk samples were fortified at 0.1 ppm.
[b] NA indicates not analyzed.

These data indicate that mancozeb (fortified samples) was stable for only 1 month in potatoes, for up to 4 months in dry beans, frozen corn, lettuce, and for up to 6 months in tomatoes, meat, and milk. The Agency concluded that ETU was stable for three months or longer in coarsely ground fortified samples of dry beans, corn, meat, milk, and tomatoes; 2 months in lettuce; and 0.5 months in potatoes. In finely ground fortified samples, ETU was stable 12 days in dry beans, frozen corn, lettuce, tomato, and meat; but ETU was stable for only 5 days in potatoes.

Rohm and Haas Company (1991; MRID 41976101; CBRS No. 8513) submitted data from a study performed by Enviro-Bio-Tech Ltd. pertaining to storage stability of mancozeb and ETU in or on apples. A group of 100 whole apples were sprayed with 1,000 ppm ai solution of mancozeb in acetone (80% WP formulation); this rate is equivalent to 1.2 lb ai/A. A second group of 100 whole apples were sprayed with a 100 ppm ai solution of ETU in water; this rate is equivalent to 0.12 lb ai/A. After spraying, the apples were allowed to air-dry for one hour, separated into subsamples of seven apples each, and stored in a freezer at -18 to -20 C. An identical number of untreated apples were stored frozen for each subsample. Samples were shipped frozen the same day as treatment and stored at -20 C (±5 C) upon receipt at the laboratory and were kept frozen until analyzed, except for day-0 samples which were analyzed the same day as received. Untreated apples were immediately analyzed to confirm the initial absence of mancozeb and ETU, and were fortified with mancozeb at 0.05-2 ppm or with ETU at 0.01-0.1 ppm. The stored apples were removed from storage one day prior to analysis, thawed for 10 minutes, homogenized with dry ice, and returned to frozen storage for 24 hours prior to analysis. Apples were removed from frozen storage

at intervals of 14, 30, 61, 121, 183, 365, and 548 days. The method recoveries of mancozeb and ETU from fortified, untreated apple homogenates were conducted at each analysis date. Mancozeb analyses were conducted using a colorimetric method (Pease, as modified by Keppel; JAOAC, 54:528-532); ETU analyses were conducted using a GC/FPD method (Onley; JAOAC, 60:1105-1110). The limit of detection was 0.05 ppm for mancozeb and 0.01 ppm for ETU. Data pertaining to the storage stability of residues of mancozeb and ETU are presented in Table 41; the method recoveries of mancozeb and ETU from fortified apple samples at each sampling date are presented in Table 42.

Table 41. Storage stability of mancozeb and ETU in or on whole apples fortified with mancozeb and ETU.

	Mancozeb-treated			ETU-treated	
Storage (days)[a]	Mancozeb ppm[b]	Rec. (%)[c]	ETU ppm[b]	ETU ppm[b]	Rec. (%)[c]
0	1.68		0.032	0.072	
15	1.64	97.6	0.046	0.048	67.0
31	1.68	100	0.057	0.062	86.6
62	1.72	102	0.034	0.038	53.1
122	1.90	113	0.035	0.032	44.7
184	1.68	100	0.020	0.010	14.0
366	1.70	101	0.038	<0.01(ND)	-
549	1.61	95.8	0.030	<0.01(ND)	-

[a] Includes one day of frozen storage after homogenization of sample in dry ice.
[b] The results, calculated by study reviewer from the raw data, represent an average of duplicate aliquots from one subsample and were not corrected for method recoveries.
[c] Percent recoveries calculated by study reviewer from the raw data using the day-0 samples as 100% recovery. Conversion factor (percent) in parentheses.

Table 42. Method recoveries from stored, frozen, untreated apples fortified with mancozeb or ETU and analyzed concurrently with the storage stability samples.

Storage (days)[a]	Mancozeb Fort. (ppm)	Mancozeb Recovery (%)	ETU Fort. (ppm)	ETU Recovery (%)
0	0.05	84	0.01	89,116
	2	92	0.1	89,109
15	2	91,93	0.05	82,88
31	2	94,95	0.05	76,86
62	2	95,95	0.05	92,104
122	2	94,96	0.05	96,104
184	2	98,98	0.05	92,96
366	2	97,99	0.05	78
549	2	97,100	0.05	82,82

[a] Includes one day of frozen storage after homogenization of sample in dry ice.

The data presented in previous tables indicate that residues of mancozeb (fortified samples) were stable in or on whole apples treated with mancozeb for up to 549 days. Frozen storage stability of ETU residues in or on whole apples treated with mancozeb could not be determined because percent recoveries (based on day-0 residue data) were quite variable. Recoveries of ETU from mancozeb-fortified samples ranged from 63% (day 184) to 180% (day 31). Residues of ETU were stable for up to 31 days in or on whole apples treated with ETU.

MAGNITUDE OF THE RESIDUE IN PLANTS

The Mancozeb Guidance Document, dated 4/87, required additional crop field trials depicting residues of mancozeb, ETU and other residues of concern in or on apples, asparagus, bananas, carrots, celery, corn, cottonseed, cranberries, cucumbers, fennel, grapes, melons, onions, papayas, peanuts, pears, potatoes, sugar beet (roots and tops), summer squash, tobacco, tomatoes, and wheat. Additional data are also required for processed products of corn, cottonseed, grapes, peanuts, potatoes, and sugar beets. The Guidance Document also required residue data and proposal of tolerances to support registered seed or planting/propagation stock uses on caprifigs, flax, pineapples, rice, safflower, and sorghum.

According to the EBDC PD 4, only certain food/feed uses of mancozeb will be allowed, provided label revisions and residue data requirements are submitted. The food/feed uses of mancozeb allowed by the EBDC PD 4 are listed in Table 43. As a result of

the EBDC PD 4 ruling, the use of mancozeb on carrots and celery will no longer be allowed.

In response to the Guidance Document requirements, the Mancozeb Task Force submitted data for apples, asparagus, bananas, carrots, corn, cucumbers, cranberries, grapes, onions, papayas, peanuts, pears, potatoes, sugar beets, tomatoes, wheat, and crops with seed treatments. These submissions are detailed by topic in the "INTRODUCTION" section of this Update document.

The Mancozeb Task Force, has offered some of the listed data submissions, in whole or in part, to support a petition (1989; PP#9F3816) for the reduction of tolerances for residues of mancozeb in or on wheat grain (from 5 ppm to 1 ppm), wheat bran (from 20 ppm to 1 ppm), grapes (from 7 ppm to 3 ppm), peanuts (from 0.5 ppm to 0.1 ppm), and sugar beets (from 2 ppm to 1 ppm) and the establishment of a permanent tolerance for potatoes (from the interim tolerance of 0.5 ppm to 0.1 ppm). The Agency has reviewed this petition in a memorandum by S. Hummel (CBRS No. 5964 dated 10/12/90) who concluded that the evaluation of these proposed tolerance revisions will require resubmission of the petition to include Sections A, B, and C.

The Mancozeb Task Force members separately submitted applications/proposals to amend their product labels to incorporate maximum number of applications and restore mancozeb uses on other crops. These applications were reviewed by S. Hummel (CB Nos. 8439, 8413, 9110, and 9115 dated 1/22/92; CB Nos. 8536-8 and 8441-3 dated 1/28/92; and CB Nos. 8571, 8410, 8411, 8992, 8993, 8995, 9097, 9098, and 9001 dated 1/28/92. These applications are now superseded by the EBDC PD 4.

Since issuance of the Guidance Document, the intrastate registrations for the 5.6% D formulation (EPA Reg. No. 31143-4466) in TX and the 4.8% D formulation (EPA Reg. No. 6023-3043) in CA have been canceled. Rohm and Haas has stated that they have no mancozeb registrations for D formulation and therefore, they do not intend to submit data reflecting this formulation class (EPA Memorandum CBRS No. 4015, S. Hummel, dated 9/27/88). CBRS concluded that no data reflecting the D formulation will be required, provided <u>all</u> dust uses are canceled. The Mancozeb Guidance Document data requirements for crop field trials using D formulations remain outstanding for food/feed use sites for which dust formulations are still registered (potatoes, tomatoes, and cucumbers). Registrants, other than members of the Task Force or other interested parties, who wish to retain the use patterns reflecting D formulation should be informed that additional data are required.

Table 43. Mancozeb uses allowed by the EBDC PD 4.

Crop	Rate (lb ai/A)	Maximum No. Applns.	Minimum Appln. Int. (days)	Minimum PHI (days)
Apples[a]				
-prebloom	4.8	4	7	bloom
-extended	2.4	7	7	77
Asparagus	1.6	4	10	180 120 CA/AZ
Bananas	2.4	10	14	0
Barley	1.6	3	7	26
Corn, field	1.2	10	--	40
Corn, sweet and pop				
-East of MS River, AR and LA	1.2	15	4	7
-West of MS River, except AR and LA	1.2	5	4	7
Cotton	1.6	4	--	May not be applied after bolls open
Crabapples/Quince[a]				
-prebloom	4.8	4	7	bloom
-extended	2.4	7	7	77
Cranberries	4.8	3	7	30
Cucumbers	2.4	8	7	5
Fennel	1.6	8	7	14
Grapes				
-East of Rocky Mtns.	3.2	6	7	66
-West of Rocky Mtns., except CA	2	3	7	66
-CA	2	3	7	bloom
Melons	2.4	8	7	5
Oats	1.6	3	7	20
Onions, dry bulb[b]	2.4	10	7	7
Papayas	2	14	14	0
Peanuts	1.6	8	7	14
Pears[a]				
-prebloom	4.8	4	7	bloom
-extended	2.4	7	7	77
Potatoes	1.6	7	5	14 3 in CT, FL, MA, ME, NH, NY, PA, VT, and WI
Rye	1.6	3	7	26
Squash, summer	2.4	8	7	5
Sugar beets	1.6	7	7	14
Tomatoes				
-West of MS	1.6	4	7	5
-East of MS	2.4	7	7	5
Wheat	1.6	3	7	26

[a] Treatment schedules may not be combined or integrated.
[b] Application to exposed bulbs is prohibited.

Rohm and Haas submitted a summary (MRID 40258301) of previously submitted data comparing ground and aerial applications. Currently, the Agency no longer requires crop field trials reflecting aerial application in cases where adequate data are available from the use of ground equipment reflecting the same application rate, number of applications, and preharvest intervals, provided that the product label specifies aerial applications are to be made in a minimum of 2 gal/A of (or 10 gal/A in the case of tree crops). See CB memorandum dated 12/6/91 by R. Quick (Requirements for Crop Field Trials to Support Aerial Applications).

The Guidance Document required storage stability data to reflect the storage intervals of all raw and processed commodity samples analyzed for mancozeb, ETU, and other residues of concern. The Agency (EPA Memorandum CBRS No. 7134, S. Hummel, dated 11/26/90) noted differences and variability in the stability of ETU in frozen storage which were attributed to many factors including the specific commodity, storage conditions, and sample handling. As a result, the Agency requires that storage stability studies must be concurrently conducted with the residue field trial studies. The availability of these storage stability data are noted in each crop section.

The use patterns discussed in the following sections include only those end-use products registered to the Mancozeb Task Force [Rohm and Haas, Ciba-Geigy, E. I. du Pont, and Atochem (formerly Pennwalt)]. The registered uses are based on the product labels of the above listed registrants according to the EPA Site Listing (SPO5) dated 9/25/90. A list of mancozeb end-use products along with the formulation classes registered to the Task Force is presented in Table 44.

Table 44Mancozeb end-use products registered to Atochem (formerly Pennwalt), Ciba-Geigy, E.I. du Pont, and Rohm and Haas.

Registrant	Formulation	EPA Reg. No.	Accepted Date
Ciba-Geigy	48% WP	100-629	01/09/90
Ciba-Geigy	70% WP	100-689	12/01/88
E.I. du Pont	37% FlC	352-398	12/28/89
E.I. du Pont	80% FlC	352-341	12/28/89
E.I. du Pont	75% DF	352-449	12/28/89
Atochem	62% WP	4581-358	03/26/90
Atochem	75% DF	4581-370	04/26/90
Rohm & Haas	70% DF	707-179	12/28/89
Rohm & Haas	75% DF	707-180	02/08/88
Rohm & Haas	32% FlC	707-162	01/17/83
Rohm & Haas	37% FlC	707-156	02/08/88
Rohm & Haas	80% WP	707-78	02/08/88
Rohm & Haas	80% WP	707-97	01/04/83

The use patterns and residue data discussed in this Update are based on the current labels and data submissions made by the Mancozeb Task Force. When end-use products DCIs are developed (e.g. at the issuance of RED), RD should require that <u>all</u> end-use product labels (e.g. any unamended basic producer labels, SLNs, and products covered under generic data exemption) be amended such that they are consistent with basic producer labels.

<u>Root and Tuber Vegetables Group</u>

<u>Carrots</u>

<u>Conclusions</u>:

The EBDC PD 4 does not allow continued use on carrots. All carrot uses must be deleted from product labels. The following are required:

- Revised labels deleting carrots from all registered mancozeb products. No additional data are required for carrots, provided use directions for carrots are deleted from all mancozeb labels. If, however, any use on carrots is continued for any reason, then full supporting residue data will be required for the label use pattern.

<u>References (not used)</u>:

[The following reference(s) pertain to uses of mancozeb which are no longer allowed by the EBDC PD 4.]

MRID(s): 40869703.

Discussion of the data:

N/A.

Potatoes

Tolerance(s):

An interim tolerance of 1 ppm has been established for the coordination product of zinc ion and maneb (calculated as zinc ethylenebisdithiocarbamate) in or on potatoes [40 CFR §180.319].

Use directions and limitations:

The 32 and 37% FlC, 37-80% WP, 70 and 75% DF formulations are registered for multiple foliar applications to potatoes at 0.6-1.6 lb ai/A on a 7- to 10-day interval using either ground or aerial equipment. These formulations are also registered for seed piece treatment at 0.78-1 lb ai/50 gal water. The 48 and 70% WP formulation (Ciba-Geigy EPA Reg. Nos. 100-629 and 100-689, respectively) specify a 7-day PHI. A maximum of four applications/season (totalling 4 lb ai/A), and a maximum seasonal use rate of 22.4 lb ai/A are specified for the respective 48 and 70% WP formulations. Except for the 48 and 70% WP formulations, no PHI, maximum number of applications, or maximum seasonal use rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for potatoes must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 5 days, and a minimum PHI of 14 days. A PHI of 3 days is allowed in CT, FL, MA, ME, NH, NY, PA, VT, and WI. Labels must state that use is recommended within an IPM program, and that vine kill should occur 14 days before harvest.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on potatoes harvested following multiple foliar applications of the WP and D formulations. In addition, the Guidance Document required revision of labels to specify the maximum seasonal rate or the maximum number of applications/season and establish a PHI. Processing studies were also required.

The earlier potato residue data discussed in the Residue Chemistry Chapter were inadequate because the treatments did not

reflect the maximum use pattern and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Potato samples were stored 4 to 85 days before analysis for mancozeb and 9 to 144 days before analysis for ETU. Samples from only one site (OH) were analyzed for ETU within 2 weeks of harvest (the time ETU remains stable in potatoes).

In response to the Guidance Document, the Mancozeb Task Force submitted field residue data (MRIDs 40913301 and 41091601) from tests conducted in CA and ID. Residue data from CA cannot be used to fulfill the requirements for reregistration since the potato samples from this test location were stored frozen for 307-324 days prior to analysis for mancozeb and for 309-326 days prior to analysis for ETU. The available storage stability data indicate that residues of mancozeb are only stable for up to one month and ETU residues are only stable for up to two weeks in or on potatoes.

Residue data from ID may be used to support the requirements for reregistration; the tests are supported by storage stability data and were conducted according to the use patterns allowed by PD 4. Residues of mancozeb were <0.05(nondetectable)-0.20 ppm, (which are below the interim tolerance of 1 ppm) in or on potatoes harvested 1 day following the last of five or six foliar applications at 1-15x the maximum single application rate or 0.9-11x the maximum seasonal application rate allowed by PD 4. Residues of ETU were <0.01 ppm (nondetectable) in or on these same samples. The submitted field residue data, however, do not fulfill the requirements for reregistration because geographical representation of adequate data is lacking. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum or 7 applications or 11.2 lb ai/A/season, a minimum application interval of 5 days, and a minimum PHI of 14 days. A PHI of 3 days is allowed in CT, FL, MA, ME, NH, NY, PA, VT, and WI. Additionally, labels must state that use is recommended within an IPM program, and that vine kill should occur 14 days before harvest.

- Data depicting mancozeb, ETU, and other residues of concern in or on potatoes harvested 3 days following the last of 7 applications at 1.6 lb ai/A/application at 5-day intervals. Tests must be conducted in CO(6%), ME(6%), OR(6%), WA(18%), and WI(6%); these states along with ID(28%) where data are available accounted for ca. 70% of the 1988 U.S. potato production (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

Samples must be frozen immediately after harvest and analyzed within two weeks of harvest.

The Mancozeb Task Force also submitted a processing study (MRID 41091601) depicting residues of mancozeb and ETU in the processed commodities of potatoes following treatment at 2 and 9x the maximum seasonal application rate allowed by PD 4. The available processing data indicate that residues of mancozeb concentrate in chips and dehydrated flakes, and that mancozeb residues are converted to ETU in dehydrated flakes, peels, and granules. Concentration factors could not be calculated, since residues were nondetectable in potatoes prior to processing. The processing data do not satisfy data requirements because (i) no data were submitted depicting residues in or on dry peels; (ii) no method recovery data were submitted for mancozeb residues in or on whole raw potatoes and in granules, or for ETU in granules; and (iii) no storage stability data were submitted from the performing laboratory, the National Food Laboratory; the limit of detection used in the processing study was four times higher than the limit of detection previously reported. The following data remain outstanding:

- Data depicting the potential for concentration of mancozeb, ETU, and other residues of concern in chips, granules, and wet and dry peel from potatoes bearing measurable weathered residues. If residues concentrate/convert in processed products, then appropriate food/feed additive tolerance must be proposed.

References (used):

MRID(s): 40913301. 41091601.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40913301 and 41091601) submitted data from four tests conducted in CA(1) and ID(3) pertaining to residues of mancozeb and ETU in or on potatoes following five or six foliar applications of the 80% WP formulation at 1.6, 8, and 24 lb ai/A/application (1, 5, and 15x the maximum single application rate allowed by PD 4) using ground (ID) and aerial (CA) equipment. The results are presented below.

State	No. of Applns. (G/A)	Rate (lb ai/A)	PTI (days)	Residues (ppm)[a] Mancozeb	ETU	Maximum Storage (days)
CA	1+4 (A)	1.6+2.4 = 11.2	0	<0.05	<0.01	326
CA	1+4 (A)	1.6+2.4 = 11.2	0	<0.05	<0.01	326
CA	1+4 (A)	1.6+2.4 = 11.2	5	<0.05	0.01	326
CA	1+4 (A)	1.6+2.4 = 11.2	5	<0.05	0.02	326
CA	1+4 (A)	1.6+2.4 = 11.2	15	<0.05	0.03	326
CA	1+4 (A)	1.6+2.4 = 11.2	15	<0.05	0.02	326
ID	6 (G)	1.6 = 9.6	1	<0.05	<0.01	15
ID	6 (G)	8.0 = 48.0	1	0.20	<0.01	15
ID	5 (G)	24.0 = 120.0	1	<0.05	<0.01	15

[a] Three samples each from CA and ID; reported values reflect duplicate analyses on each of three samples from CA.

Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on two untreated samples. Recoveries were 93% from one sample (ID test) fortified with mancozeb at 0.1 ppm, and 83 and 111% from two samples fortified with ETU at 0.05 and 0.01 ppm; reported residues were corrected for these recovery values. Recoveries were 87% from one sample (CA test) fortified with mancozeb at 0.05 ppm, and 93% from one sample fortified with ETU at 0.01 ppm; reported residues were corrected for these recovery values. Samples from ID were stored frozen (-20 C) for 13-15 days prior to analysis by Enviro-Bio-Tech, Ltd. Samples from CA were stored frozen (-10 C) for 307-324 days prior to analysis for mancozeb and for 309-326 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. Storage stability data pertaining to these storage intervals and conditions are available; see "STORAGE STABILITY DATA" section. These data indicate that residues of mancozeb are only stable for up to one month and ETU residues are only stable for up to two weeks in or on potatoes. Based on this information, only data from ID are supported by storage stability data since the potato samples from this test location were stored frozen for only 13-15 days prior to analysis.

The Mancozeb Task Force (1990; MRID 41091601) submitted data from a single study conducted in OH pertaining to residues of mancozeb and ETU in the processed products of potatoes. Potato tubers were harvested one day following the last of 13 foliar applications (using aerial equipment) of the 80% WP formulation

at 1.6 or 8 lb ai/A/application (1 or 5x the maximum single application rate, or 2 or 9x the maximum seasonal application rate allowed by PD 4). Residues of mancozeb and ETU were nondetectable (<0.2 and <0.02 ppm, respectively) in or on four samples of tubers treated at 1x and 5x. The raw unwashed potatoes were washed and processed according to simulated commercial procedures into peeled tubers (using abrasion or hand methods), peels (wet), chips, granules, and dehydrated flakes. The results are presented below.

Item	Residues (ppm)			
	Mancozeb	ETU	Mancozeb	ETU
	1x		5x	
Potatoes	<0.2	<0.02	<0.2	<0.02
Dehy. flakes	0.58-0.67[a]	0.03-0.17[b]	<0.2	0.1-0.39[c]
Chips	<0.2	<0.02	0.26-0.3[d]	<0.02
Peeled potatoes	<0.2	<0.02	<0.2	0.02-0.03[e]
Wet peels	<0.2	<0.02	<0.2	0.02-0.03[e]
Granules	<0.2	<0.02	<0.2	0.07-0.09[f]

[a] Concentration factor ≥2.9-3.4x.
[b] Conversion factor ≥5-75%; calculated as follows:
[(ETU product - ETU RAC)/Mancozeb RAC] x 100 = % Conversion.
[c] Conversion factor ≥40-185%.
[d] Concentration factor ≥1.3-1.5x.
[e] Conversion factor ≥0-5%.
[f] Conversion factor ≥25-35%.

Apparent residues of mancozeb and ETU were nondetectable (<0.2 and <0.02 ppm, respectively) in or on one untreated tuber sample and in one sample each of the processed products. Mancozeb analyses were conducted using a modified colorimetric method (Keppel) with a limit of detection of 0.2 ppm; ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.02 ppm. Recoveries were 92% from one sample of washed and peeled tubers, 63-79% from three samples of wet peels, and 58 and 79% from two samples of dehydrated flakes fortified with mancozeb at 0.24-0.56 ppm. Recoveries were 53 and 83% from two samples of unwashed whole tubers and 79 and 91% from two samples of peels fortified with ETU at 0.02 and 0.1 ppm. Samples were stored frozen for 152-244 days prior to analysis for mancozeb and ETU by the National Food Laboratory in Washington, DC. No concurrently conducted storage stability data were submitted to support this study.

Geographic representation of adequate data is lacking since the test state of ID only accounted for (28%) of the 1988 U.S. potato production (Agricultural Statistics Board, NASS, USDA Crop

Database, Aug. 1989). Residue data from a single test conducted in CA cannot be used to fulfill the requirements for reregistration since the potato samples from this test location were stored frozen for 307-324 days prior to analysis for mancozeb and for 309-326 days prior to analysis for ETU. The available storage stability data indicate that residues of mancozeb are only stable for up to one month and ETU residues are only stable for up to two weeks in or on potatoes.

Residue data collected from tests conducted in ID may be used to support the requirements for reregistration; the tests are supported by storage stability data and were conducted according to the use patterns allowed by PD 4. Residues of mancozeb were <0.05(nondetectable)-0.20 ppm, (which are below the interim tolerance of 1 ppm) in or on potatoes harvested 1 day following the last of five or six foliar applications at 1-15x the maximum single application rate or 0.9-11x the maximum seasonal application rate allowed by PD 4. Residues of ETU were <0.01 ppm (nondetectable) in or on these same samples. The submitted field residue data, however, do not fulfill the requirements for reregistration because geographical representation of adequate data is lacking. Additional field residue data from other potato-growing regions are required.

The available processing data indicate that residues of mancozeb concentrate in chips and dehydrated flakes, and that mancozeb residues are converted to ETU in dehydrated flakes, peels, and granules. Concentration factors could not be calculated, since residues were nondetectable in potatoes prior to processing. The processing data do not satisfy data requirements because no data were submitted depicting residues in or on dry peels and no method recovery data were submitted for mancozeb in whole raw potatoes and granules or for ETU in granules. In addition, no storage stability data were submitted from the performing laboratory, the National Food Laboratory; the method limit of detection used in the processing study was four times higher than the limit of detection previously reported. Additional processing data are required.

Sugar beets

Tolerance(s):

A tolerance of 2 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on sugar beet roots [40 CFR §180.176].

Use directions and limitations:

The 32, 37, and 80% FlC and 62 and 80% WP formulations are registered for multiple foliar applications to sugar beets at 1.2-1.6 lb ai/A/application. The 70% and 75% DF formulations are registered for the same use at 1.1-2.4 lb ai/A/application. Applications may be made using ground and aerial equipment and repeated at 7- to 10-day intervals. A 14-day PHI has been established. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for sugar beets must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on sugar beets harvested following applications of WP and D formulations using ground and aerial equipment in separate tests. In addition, the Guidance Document required revised labels specifying the maximum seasonal rate or the maximum number of applications/season. The Guidance Document also required processing data reflecting residues of concern in sugar beet pulp. According to the EPA Site Listing (SP05) dated 9/25/90, all D formulation uses on sugar beets have been canceled.

The earlier sugar beet residue data discussed in the Residue Chemistry Chapter were inadequate because the treatments did not reflect the maximum use pattern of multiple applications at 1.7 lb ai/A and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Sugar beet samples from 1985 field trials were stored 77 to 109 days before analysis for mancozeb and 65 to 197 days before analysis for ETU.

In response to the Guidance Document, Mancozeb Task Force submitted field residue data (MRID 40869712). These data indicate that residues of mancozeb did not exceed the established 2 ppm tolerance when harvested 1 or 15 days following treatments at 0.6x the maximum seasonal application rate allowed by PD 4. Residues of ETU were nondetectable (<0.01 ppm) in or on six samples from these same tests. The available data do not fulfill the requirements for reregistration because tests were not

conducted according to the maximum use pattern allowed by PD 4, geographical representation is inadequate, and no processing data were submitted. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

References (used):

MRID(s): 40869712.

Discussion of the data:

The Mancozeb Task Force (1988; MRID 40869712) submitted data from a single test conducted in ID pertaining to residues of mancozeb and ETU in or on sugar beet roots harvested 15 and 29 days following the last of four foliar applications (using ground equipment) of the 80% WP formulation at 1.6 lb ai/A/application (1x the maximum single application rate, 0.6x the maximum seasonal application rate allowed by PD 4). Residues of mancozeb were 0.057 and 0.076 ppm in or on two samples harvested 1 day posttreatment, and <0.05 ppm (nondetectable) in or on four samples. Residues of ETU were <0.01 ppm (nondetectable) in or on six samples. Reported residue values were corrected for method recovery using 82% for mancozeb and 93% for ETU. Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on one untreated sample. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 68% from one sample fortified with mancozeb at 0.05 ppm, and 97% from one sample fortified with ETU at 0.01 ppm. Samples were stored frozen (-10 C) for 286-314 days prior to analysis for mancozeb and for 286-322 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. Based on storage stability data for mancozeb and ETU on potatoes, residues would be expected to be stable in sugar beets stored frozen for 2 weeks.

Considering the newly submitted field trial data along with data reviewed in the Residue Chemistry Chapter, geographic representation is adequate since the test states of CA, TX, ID, and MN, along with neighboring states accounted for about 80% of the 1988 U.S. sugar beet production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data fulfill the requirements for reregistration because tests were conducted at the maximum use pattern allowed by PD 4, geographical representation is adequate. No processing data were submitted, however, a processing study was reviewed in the Residue Chemistry Chapter. Two samples were processed. Residues of mancozeb and

ETU did not concentrate in sugar beet molasses or white sugar. One sample of sugar beet pulp had residues of mancozeb 3x higher than in the rac. A feed additive tolerance is required. No additional data are required.

Leaves of Root and Tuber Vegetables Group

Sugar beet tops

Tolerance(s):

A tolerance of 65 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on sugar beet tops [40 CFR §180.176].

Use directions and limitations:

The 32, 37, and 80% FlC and 62 and 80% WP formulations are registered for multiple foliar applications to sugar beets at 1.2-1.6 lb ai/A/application. The 70% and 75% DF formulations are registered for the same use at 1.1-2.4 lb ai/A/application. Applications may be made using ground and aerial equipment and repeated at 7- to 10-day intervals. A 14-day PHI has been established. No maximum number of applications per season or maximum seasonal application rate has been established. Treated tops may not be fed to livestock. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for sugar beets must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on sugar beet tops harvested following multiple foliar applications (using ground and aerial equipment in separate tests) of the WP or FlC, and D formulations. In addition, the Guidance Document required revised labels specifying the maximum seasonal rate or the maximum number of applications/season. According to the EPA Site Listing (SPO5) dated 9/25/90, all D formulation uses on sugar beets have been canceled.

in the Residue Chemistry Chapter dated 9/10/86 indicating that mancozeb residues concentrated 2x in flour, 4x in bran, and 4x in shorts, and that ETU residues were nondetectable (<0.01 ppm) in the processed products.

The earlier wheat residue data discussed in the Residue Chemistry Chapter were inadequate because of inadequate geographic representation and lack of information on length and conditions of sample storage. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage for wheat milling samples only. Data reflecting the PD 4 use pattern are available only from AL.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRIDs 40869715, 40869716, and 41092005) depicting residues of mancozeb and ETU in or on wheat grain. The available data indicate that residues of mancozeb will not exceed the established tolerance in or on wheat grain harvested 25-56 days following treatment at 1x the maximum seasonal application rate allowed by PD 4. Residues of ETU were nondetectable (<0.01 ppm) in or on wheat grain samples from these same tests. The submitted data do not satisfy the requirements for reregistration because wheat grain samples were not harvested at the minimum PHI. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 3 applications or 4.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 26 days.

- Data depicting mancozeb, ETU, and other residues of concern in or on wheat grain harvested 26 days following the last of three applications of a representative WP, FlC, or DF formulation at 1.6 lb ai/A/application at 7-day intervals. Tests must be conducted in CO(4%), IL(4%), KS(18%)/MO(4%)/NE(4%), ND(6%), OK(10%)/TX(5%), and WA(7%)/OR(3%)/ID(4%), since these states accounted for ca. 70% of the 1988 U.S. production of wheat (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

References (used):

MRID(s): 40869715. 40869716. 41092005.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40869715, 40869716, and 41092005) submitted data from a four tests conducted in MO, OK, OR, and TX pertaining to residues of mancozeb and ETU in or on wheat grain harvested 25-56 days following the last of 2-3 foliar applications of the 80% WP formulation at 1.6 or 2.4 lb

ai/A/application (1x the maximum seasonal application rate allowed by PD 4) using ground and aerial equipment. Residues of mancozeb and ETU are presented in the table below.

Location[a] (G/A)	PHI (days)	No. of Applns = rate[b]	Residues (ppm)[c] Mancozeb Range	ETU Range	Maximum Storage (days)
MO(G)	36	3(1.6) = 4.8	<0.05	<0.01	74
TX(A)	46	3(1.6) = 4.8	0.06-0.12	<0.01	86
OK(A)	56	3(1.6) = 4.8	<0.05-0.12	<0.01	86
OR(A)	25	2(2.4) = 4.8	0.95-0.99	<0.01	483

[a] G/A = Ground or aerial equipment.
[b] Rate in lb ai/A.
[c] Residue values were corrected for average method recovery of 73%(MO, TX, and OK) and 95%(OR) for mancozeb; and 102%(MO), 87%(OK and TX), and 97%(OR) for ETU. Ranges reflect two samples.

Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on four untreated samples. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 73-96% from three samples fortified with mancozeb at 0.05-1 ppm, and 87-102% from three samples fortified with ETU at 0.01-0.02 ppm. Samples were stored frozen for 74-483 days prior to analysis by Enviro-Bio-Tech, Ltd. Storage stability data pertaining to these storage intervals and conditions are available; however, the data indicate that residues of ETU are only stable for up to six months in or on wheat grain (see "STORAGE STABILITY DATA" section). Samples from OR (the location treated with the use most closely corresponding to the PD 4 use pattern) were stored more than 12 months. Residues of ETU in wheat declined to 60% of the original amount after 24 months.

Geographic representation is adequate since the test states of MO(4%), OK(10%), OR(3%), and TX(5%) and neighboring states of AR(3%), CA(2%), CO(4%), ID(4%), IL(4%), KS(18%), KY(1%), LA(1%), NE(4%), TN(1%), WA(7%) account for ca. 70% of the 1988 U.S. wheat production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data indicate that residues of mancozeb will not exceed the established tolerance in or on wheat grain harvested 25-56 days following treatment at 1x the maximum seasonal application rate allowed by PD 4. However, the submitted data do not satisfy the requirements for reregistration because wheat grain samples were not harvested at the minimum PHI.

Forage, Fodder, and Straw of Cereal Grains Group

Corn (field) forage, fodder, and silage

Tolerance(s):

Tolerance(s) of 5 ppm have been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on corn fodder and corn forage [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered for multiple foliar applications to hybrid and field corn at 1.1-1.2 lb ai/A/application using ground or aerial equipment. Applications may be repeated as needed at 4-14 day intervals. A 40-day PHI has been established. The 80% WP, 32, 37, and 80% FlC, and 70% and 75% DF formulations are also registered for seed treatment of field corn at 0.13-0.27 lb ai/100 lb seed. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for field corn must be revised to specify a maximum application rate of 1.2 lb ai/A/application, a maximum of 10 applications or 12 lb ai/A/season, and a minimum PHI of 40 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required field data depicting residues in or on field corn forage and fodder following treatment with the 80% WP and 3.2% D formulations. In addition, the Guidance Document required the registrant(s) to propose label revisions establishing a maximum seasonal use rate or maximum number of applications per season. Since issuance of the Guidance Document, use of the 3.2% D formulation on field corn has been canceled.

The earlier residue data on field corn forage and fodder discussed in the Residue Chemistry Chapter were inadequate because the treatments did not reflect the maximum use pattern, geographic representation was inadequate and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas

reported the length, but not the conditions of storage. Field corn samples were stored 97 to 622 days before analysis (all but one sample stored less than 265 days). Data matching the PD 4 use pattern were available from FL.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRID 40869705) depicting residues of mancozeb and ETU in or on field corn stover (fodder). The available data indicate that the established tolerance for corn fodder may be too low. Residues exceeded the established tolerance (up to 12.6 ppm) in or on two samples of field corn fodder harvested 54 days following treatment at 0.7x the maximum seasonal application rate allowed by PD 4. Residues of ETU were <0.01(ND) and 0.08 ppm in or on these same samples. The submitted data do not satisfy the requirements for reregistration for the following reasons: (i) no data were submitted reflecting treatment at the maximum seasonal application rate and minimum PHI allowed by PD 4; (ii) no data were submitted depicting residues in or on corn forage; and (iii) geographic representation is inadequate. No concurrently conducted storage stability studies were submitted to support these data. The registrant may have to propose a higher tolerance for residues of mancozeb in or on field corn fodder, upon receipt of appropriate residue data.

The following additional data are required:

- Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, a maximum of 10 applications or 12 lb ai/A/season, and a minimum PHI of 40 days.

- Data depicting mancozeb, ETU, and other residues of concern in or on field corn forage and fodder harvested 40 days following the last of ten applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A/application. Tests must be conducted in IL(14%), IN(8%), IA(18%), MN(7%), NE(17%), and OH(5%) since these states accounted for ca. 70% of the 1988 U.S. production of field corn (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

References (used):

MRID(s): 40869705.

Discussion of the data:

The Mancozeb Task Force (1988; MRID 40869705) submitted data from one test conducted in HI pertaining to residues of mancozeb and ETU in or on field corn stover (fodder) harvested 54 days following the last of seven foliar applications (using ground equipment) of the 80% WP formulation at 1.2 lb ai/A/application (1x the maximum single application rate allowed by PD 4; 0.7x the

maximum seasonal application rate allowed by PD 4). Residues of mancozeb were 10.1 and 12.6 ppm; residues of ETU were <0.01 (nondetectable; ND) and 0.08 ppm in or on two samples. Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on one untreated sample. Reported residue values were corrected for method recovery using 79% for mancozeb and 87% for ETU. Mancozeb analyses were conducted using a colorimetric method (Keppel) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 95% from one sample fortified with mancozeb at 10 ppm, and 74% from one sample fortified with ETU at 0.1 ppm. Samples were stored for 109 days prior to analysis for mancozeb and for 44 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data. Residues of mancozeb and ETU in lettuce were stable up to two months in frozen storage.

Geographic representation for field corn stover is inadequate since the test state of HI accounted for <1% of the 1988 field corn production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data indicate that the established tolerance for corn stover (fodder) may be too low. Residues exceeded the established tolerance in or on field corn fodder (up to 12.6 ppm) in or on two samples of field corn fodder harvested 54 days following treatment at 0.7x the maximum seasonal application rate allowed by PD 4. Residues of ETU were <0.01(ND) and 0.08 ppm in or on these same samples. The submitted data do not satisfy the requirements for reregistration for the following reasons: (i) no data were submitted reflecting treatment at the maximum seasonal application rate and minimum PHI allowed by PD 4; (ii) no data were submitted depicting residues in or on corn forage; and (iii) geographic representation is inadequate. No concurrently conducted storage stability studies were submitted to support these data. Additional data are required.

Corn (sweet and pop) forage, fodder, and silage

Tolerance(s):

Tolerance(s) of 5 ppm have been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on corn fodder and corn forage [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered for multiple foliar applications to

pop and sweet corn at 1.1-1.2 lb ai/A/application using ground or aerial equipment. Applications may be repeated as needed at 4-7 day intervals. A 7-day PHI has been established. Treated popcorn and sweet corn forage or fodder may not be grazed or fed to livestock. The 80% WP, 32, 37, and 80% FlC, and 70% and 75% DF formulations are also registered for seed treatment of field corn at 0.13-0.27 lb ai/100 lb seed. No maximum number of applications per season or maximum seasonal application rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for sweet corn and popcorn East of the Mississippi River and in AR and LA must be revised to specify a maximum application rate of 1.2 lb ai/A/application, a maximum of 15 applications or 18 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days; and all labels bearing use directions for sweet corn and popcorn West of the Mississippi River (except AR and LA) must be revised to specify a maximum application rate of 1.2 lb ai/A/application, a maximum of 5 applications or 6 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required field data depicting residues in or on sweet corn forage following treatment with the 80% WP and 3.2% D formulations. In addition, the Guidance Document required the registrant(s) to propose label revisions establishing a maximum seasonal use rate or maximum number of applications per season.

No data on sweet corn forage or fodder were discussed in the Residue Chemistry Chapter. No data were submitted pertaining to residues of mancozeb and ETU in or on sweet corn forage. Currently, the Agency does not consider feeding restrictions to be practical for sweet corn forage. However, in FL where sweet corn is under grower control, a feeding restriction on sweet corn forage is considered enforceable.

The following requirements remain outstanding:

- Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, maximum of 15 applications or 18 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days for sweet corn and popcorn grown east of the Mississippi River, and in AR and LA; and a maximum of 5 applications or 6 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI

of 7 days for sweet corn and popcorn grown west of the Mississippi River (except AR and LA).

- Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn and popcorn forage harvested 7 days following the last of 15 foliar applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A/application applied at 4 day intervals. Tests must be conducted in FL(8%), NY(6%), and WI(19%) since these states accounted for most of the 1988 U.S. production of sweet corn east of the Mississippi River (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

- Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn and popcorn forage harvested 7 days following the last of 5 foliar applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A/application applied at 4 day intervals. Tests must be conducted in OR (11%) and WA(14%) since these states accounted for most of the 1988 U.S. production of sweet corn west of the Mississippi River (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

References (used):

MRID(s):

References (used):

MRID(s): N/A.

Discussion of the data:

N/A.

Wheat forage and straw

Tolerance(s):

A tolerance of 25 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on wheat straw [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 32, 37, and 80% FlC, and 70 and 75% DF formulations are registered for a maximum of three foliar applications per season to wheat at 1.2-1.6 lb ai/A/application

using ground and aerial equipment. Treatments may be repeated at 7-10 day intervals. A 26-day PHI and pregrazing interval has been established. These formulations may also be used for seed treatments at 0.1-0.18 lb ai/100 lb seed. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to the members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for wheat must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 3 applications or 4.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 26 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on wheat straw following application of the WP and D formulations using ground and aerial equipment in separate tests. The Guidance Document also required proposal of a tolerance for residues in or on wheat forage and submission of appropriate supporting residue data.

The earlier residue data on wheat straw discussed in the Residue Chemistry Chapter were inadequate because the treatments did not reflect the maximum use pattern, geographic representation was inadequate and information on length and conditions of sample storage were lacking.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRIDs 40869715, 40869716, and 41092005) pertaining to residues of mancozeb and ETU in or on wheat straw. The available data indicate that the established tolerance for wheat straw may be too low. Residues exceeded the tolerance (up to 122 ppm) in or on two samples of wheat straw harvested 25 days following the last of two applications of the 80% WP formulation at 2.4 lb ai/A/application (1.5x the single and 1x the maximum seasonal application rate allowed by PD 4). Residues of ETU up to 0.13 ppm were reported. No concurrently conducted storage stability studies were submitted to support these data. None of the available data match the use pattern allowed by PD 4 because the PHIs were too long. The registrant must propose a higher tolerance for residues of mancozeb in or on wheat straw, supported by appropriate residue data. No data pertaining to residues in wheat forage were submitted. The following are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 3 applications or 4.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 26 days. The label also must

specify a 26-day pregrazing interval, and that treated seed may not be used for food or feed.

- The registrant must propose a higher tolerance for residues of mancozeb in or on wheat straw. The available data indicate residues exceeded the tolerance (up to 122 ppm) after application at 1x the maximum seasonal application rate allowed by PD 4.

- Data depicting mancozeb, ETU, and other residues of concern in or on wheat straw harvested 26 days following the last of three applications of a representative WP, FlC, or DF formulation at 1.6 lb ai/A/application at 7-day intervals. Tests must be conducted in CO(4%), ID(4%). IL(4%), KS(18%), MO(4%), NE(4%), ND(6%), OK(10%), TX(5%), and WA(7%) since these states accounted for ca. 70% of the 1988 U.S. production of wheat (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989). Samples must be analyzed within 12 months of harvest.

- The registrant must propose a tolerance for residue of mancozeb in or on wheat forage and submit supporting residue data.

References (used):

MRID(s): 40869715. 40869716. 41092005.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40869715, 40869716, and 41092005) submitted data from four tests conducted in MO, OK, OR, and TX pertaining to residues of mancozeb and ETU in or on wheat straw following the last of 2-3 foliar applications of the 80% WP formulation at 1.6 or 2.4 lb ai/A/application (for a total application of 1x the maximum seasonal application rate allowed by PD 4) using ground and aerial equipment. Results of these tests are detailed below.

Location[a] (G/A)	PHI (days)	No. of Applns = rate[b]	Residues (ppm)[c] Mancozeb Range	ETU Range	Maximum Storage (days)
MO(G)	36	3(1.6) = 4.8	3.0-4.1	0.09-0.12	74
TX(A)	46	3(1.6) = 4.8	12.8-24.9	0.06-0.11	86
OK(A)	56	3(1.6) = 4.8	0.81-0.98	0.01	86
OR(A)	25	2(2.4) = 4.8	119.0-122.0	0.10-0.13	483

[a] G/A = Ground or aerial equipment.
[b] lb ai/A.
[c] Residue values were corrected for average method recovery of 93%(MO), 92%(TX and OK), and 95%(OR) for mancozeb; and 89%(MO), 106%(TX and OK), and 97%(OR) for ETU. Ranges reflect two samples.

Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in or on four untreated samples. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 92-94% from three samples fortified with mancozeb at 4-120 ppm, and 89-109% from four samples fortified with ETU at 0.01 and 0.1 ppm. Samples were stored frozen for 74-483 days prior to analysis by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data. Storage stability data for lettuce indicate that residues of ETU are only stable for two months of frozen storage.

Geographic representation is adequate since the test states of MO(4%), OK(10%), OR(3%), and TX(5%) and neighboring states of AR(3%), CA(2%), CO(4%), ID(4%), IL(4%), KS(18%), KY(1%), LA(1%), NE(4%), TN(1%), and WA(7%) accounted for ca. 70% of the 1988 U.S. wheat production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). However, none of the available data match the use pattern allowed by PD 4. The available data indicate that the established tolerance may be too low. Residues exceeded the tolerance (up to 122 ppm) in or on two samples of wheat straw harvested 25 days following the last of two applications of the 80% WP formulation at 2.4 lb ai/A/application (1.5x the single and 1x the maximum seasonal application rate allowed by PD 4). Residues of ETU up to 0.13 ppm were reported. The registrant must propose a higher tolerance for residues of mancozeb in or on wheat straw and provide additional supporting residue data. No data pertaining to residues in wheat forage were submitted. Additional data are required.

Miscellaneous Commodities

Asparagus

Tolerance(s):

A tolerance of 0.1 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on asparagus [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 70 and 75% DF, and 32, 37, and 80% F1C formulations are registered for up to four foliar applications to asparagus at 0.74-1.6 lb ai/A using ground and aerial equipment. Applications may be repeated at 10-day intervals. Foliar treatments may only be applied after the spears have been harvested. Formulations are also registered for root dip treatments at 0.37-0.8 lb ai/100 gal of water. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for asparagus must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 4 applications or 6.4 lb ai/A/season, a minimum application interval of 10 days, and a minimum PHI of 180 days (except AZ and CA); the minimum PHI in AZ and CA is 120 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting applications of the D formulation at the maximum current use. In addition, the Guidance Document required revised labels specifying the maximum seasonal rate or the maximum number of applications/season. According to the EPA Site Listing (SP05) dated 9/25/90, all D formulation uses on asparagus have been canceled.

The earlier asparagus residue data discussed in the Residue Chemistry Chapter were inadequate because information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Asparagus samples were stored up to seven months before analysis. Data discussed in the Residue Chemistry Chapter were available from WA. The PHI

from for the WA study was much longer than the 180 days permitted by PD 4.

The Mancozeb Task Force submitted data (MRIDs 40869701 and 40869702) depicting residues of mancozeb and ETU in or on asparagus. The available data indicate that residues of mancozeb will not exceed the established 0.1 ppm tolerance in or on asparagus harvested 124 days following treatment at 1x the maximum seasonal application rate allowed by PD 4. However, the submitted data do not satisfy the requirements for reregistration because geographic representation was inadequate. The following additional data are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 4 applications or 6.4 lb ai/A/season, a minimum application interval of 10 days, and a minimum PHI of 180 days; 120 days in AZ and CA.

- Data depicting mancozeb, ETU, and other residues of concern in or on asparagus harvested 180 days following the last of 4 foliar applications of a representative WP, FlC, or DF formulation at a maximum application rate of 1.6 lb ai/A applied at 10 day intervals. Tests must be conducted in WA(37%); this state along with CA(48%), where data are available, accounted for ca. 80% of the 1988 U.S. production of asparagus (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA, June 1989, p.18). Samples must be frozen immediately after collection and analyzed with two months of harvest.

References (used):

MRID(s): 40869701. 40869702.

Discussion of the data:

The Mancozeb Task Force (1987; MRID 40869701 and 40869702) submitted data from two tests conducted in CA pertaining to residues of mancozeb and ETU in or on asparagus stalks harvested 124 days following the last of four foliar applications (using aerial equipment) of the 80% WP formulation at 1.6 lb ai/A (1x the maximum single application rate allowed by the PD 4). Residues of mancozeb were <0.05 (nondetectable;ND)-0.08 ppm and residues of ETU were <0.01(ND) ppm in or on six samples. Reported residues were corrected for method recovery using 96% for mancozeb and 98% for ETU. Apparent residues of mancozeb and ETU were <0.05(ND) ppm and <0.01(ND) ppm, respectively, in or on three untreated samples. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted

using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 94-98% from three samples fortified with mancozeb at 0.05-0.10 ppm, and were 87-98% from three samples fortified with ETU at 0.01 ppm. Samples were stored frozen (-10 C) for 292-494 days prior to analysis for mancozeb and ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data. Storage stability data in lettuce indicate that residues of ETU are stable for up to two months in frozen storage.

The single test state of CA does not provide adequate geographic representation; CA accounted for only ca. 50% of the 1988 U.S. asparagus production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, June 1989, p. 18). The available data indicate that residues of mancozeb in or on asparagus will not exceed the established 0.1 ppm tolerance following treatment at 1x the maximum seasonal application rate allowed by PD 4. However, the submitted data do not satisfy the requirements for reregistration because geographic representation was inadequate. Additional data are required.

Bananas

Tolerance(s):

A tolerance of 4 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on bananas, preharvest use only, of which not more than 0.5 ppm is in or on the pulp after the peel is removed and discarded [40 CFR §180.176].

Use directions and limitations:

The 80% WP, 37 and 80% FlC, and 70 and 75% DF formulations are registered for multiple foliar applications to bananas at 1.5-3.2 lb ai/A/application. Foliar applications may be made at 2-3 week intervals using both ground and aerial equipment. No PHI, maximum number of applications per season or maximum seasonal use rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to the members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for bananas must be revised to specify a maximum application rate of 2.4 lb ai/A/application, a maximum of 10 applications or 24 lb ai/A/season, a minimum application interval of 14 days, and a minimum PHI of 0 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required data depicting residues in or on bananas harvested immediately following the final foliar application of the WP or FlC formulations. In addition, the Guidance Document required the registrant(s) to propose label revisions establishing a maximum seasonal use rate or maximum number of applications per season.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRIDs 40913303 and 40913304) depicting residues of mancozeb and ETU in or on bananas. The available data indicate that the established tolerance may be too low. Residues exceeded (up to 1.16 ppm) the tolerance in or on banana pulp after the peel is removed following treatment at ca. 1x and 1.5x the maximum seasonal application rate allowed by PD 4. Residues of ETU were nondetectable (<0.01 ppm) in or on these same samples. In addition, the registrant must explain the detection of mancozeb residues in the untreated controls reported in MRID 40913304. ETU residues in apples were only stable for three months in frozen storage. The following additional data are required:

- Revised labels specifying a maximum application rate of 2.4 lb ai/A/application, a maximum of 10 applications or 24 lb ai/A/season, a minimum application interval of 14 days, and a minimum PHI of 0 days.

- The registrant must propose a higher tolerance for residues of mancozeb in or on bananas, supported by appropriate residue data.

- The registrant must adequately explain the presence of detectable mancozeb residues in or on untreated controls reported in MRID 40913304.

References (used):

MRID(s): 40913303. 40913304.

Discussion of the data:

The Mancozeb Task Force (1987-88; MRIDs 40913303 and 40913304) submitted data from three tests conducted in HI(2) and Honduras(1) pertaining to residues of mancozeb and ETU in or on bananas following multiple applications of the 37% FlC formulation using ground and aerial equipment. Results from these tests are presented below.

Location[a] (G/A)	PHI (days)	Total Appln. rate[b]	Residues (ppm)[c] Mancozeb Range	ETU Range	Commodity (No. of samples)
Honduras(A)	9	82	0.78-1.08	<0.01	Peel(6)
			<0.05	<0.01	Pulp(6)
			0.13-0.24	<0.01	WFrt(6)
Hawaii(G)	0	25.6	6.3-11.7	<0.01	Peel(2)
			0.30-0.45	<0.01	Pulp(2)
			0.25-0.48	<0.01	Wfrt(2)
Hawaii(G)	0	35.2	8.5-9.9	<0.01	Peel(2)
			0.81-1.16	<0.01	Pulp(2)
			0.70-1.0	<0.01	Wfrt(2)

[a] G/A = Ground or aerial equipment.
[b] Honduras: Total rate reflects 6 applications at 0.665, 29 at 1.9, and 10 at 2.28 lb ai/A; intervals between applications were 1-24 days. Hawaii: Total rate reflects 8 or 11 applications at 3.2 lb ai/A.
[c] Residue values were corrected for average method recovery.

Mancozeb analyses were conducted using a colorimetric method (Keppel) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Honduras: Mancozeb and ETU residue values were respectively corrected for average method recovery of 89 and 94% (whole fruit), 81 and 88%(pulp), and 94 and 88%(peel). Recoveries were 89% from one sample of whole fruit, 81% from one sample of pulp, and 94% from one sample of peel fortified with mancozeb at 0.05-0.3 ppm. Recoveries were 90 and 98% from two samples of whole fruit, 90 and 105% from two samples of pulp, and 85 and 90% from two samples of peel fortified with ETU at 0.05-0.25 ppm. Samples were stored for 196-199 days prior to analysis for mancozeb and ETU. Hawaii: Reported residue values for whole fruit, pulp, and peel were corrected for method recovery using 81% for mancozeb and 92% for ETU. Apparent residues of mancozeb and ETU, respectively were <0.05(ND) and <0.01(ND) ppm each in or on two untreated whole fruit, pulp, and peel samples. Two additional untreated samples bore apparent mancozeb residues of 0.36 and 0.42 ppm in or on whole fruit, 0.22 and 0.48 ppm in or on pulp, and 2.71 and 5.82 ppm in or on peel. Recoveries were 78 and 87% from two samples of whole fruit, 77 and 82% from two samples of pulp, and 79 and 85% from two samples of peel fortified with mancozeb at 0.1-5 ppm. Recoveries were 82% from one sample of whole fruit, 97% from one sample of pulp, and 94% from one sample of peel fortified with ETU at 0.01-0.04 ppm. Samples were stored for 168 days prior to analysis for mancozeb

and for 63 days prior to analysis for ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data.

Geographic representation for bananas is adequate since the test state of HI accounted for 100% of the 1988 U.S. banana production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The test country of Honduras represented 21% of the 1988 imported bananas (Foreign Agricultural Trade of the United States, Fiscal Year 1988 Supplement, CED, ERS, USDA, pp.284). The available data indicate that the established tolerance may be too low. Residues exceeded (up to 1.16 ppm) the tolerance in or on banana pulp after the peel is removed following treatment at ca. 1x and 1.5x the maximum seasonal application rate allowed by PD 4. Residues of ETU were nondetectable (<0.01 ppm) in or on these same samples. In addition, the registrant must explain the detection of mancozeb residues in the untreated controls reported in MRID 40913304. No concurrently conducted storage stability studies were submitted to support these data. ETU residues in apples were stable only three months in frozen storage.

Papayas

Tolerance(s):

A tolerance of 10 ppm has been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on the whole fruit of papayas, with no residues present in the edible pulp after the peel is removed and discarded [40 CFR §180.176].

Use directions and limitations:

The 80% WP, 32 and 37% FLC, and 70% and 75% DF formulations are registered for multiple foliar applications to papayas at 1.6-2 lb ai/A/application using ground and aerial equipment. Treatments may begin at flowering and continue at 7-14 day intervals with the applications directed to the crown and blossom area. No PHI, maximum number of applications per season or maximum seasonal use rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SPO5) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for papayas must be revised to specify a maximum application rate of 2 lb ai/A/application, a maximum of 14 applications or 28 lb

ai/A/season, a minimum application interval of 14 days, and a minimum PHI of 0 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required data depicting residues in or on the whole fruit and pulp of papayas following application of the WP or F1C and D formulations. In addition, the Guidance Document required the registrant(s) to propose label revisions establishing a maximum seasonal use rate or maximum number of applications per season. According to the EPA Site Listing (SP05) dated 9/25/90, all D formulation uses on papayas have been canceled.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRIDs 40869709 and 40869710) pertaining to residues of mancozeb and ETU in or on papayas. The available data indicate that the established tolerance may be too low. Residues of mancozeb exceeded (up to 12.6 ppm) the established tolerance in or on two samples of whole unwashed papayas harvested immediately following treatment at ca. 1x the maximum seasonal application rate allowed by PD 4. Two samples of unwashed pulp from papayas receiving the same treatment contained detectable residues of mancozeb (up to 5.0 ppm). Residues of ETU up to 0.55 ppm were reported. No concurrently conducted storage stability studies were submitted to support these data. The following are required:

- Revised labels specifying a maximum application rate of 2 lb ai/A/application, a maximum of 14 applications or 28 lb ai/A/season, a minimum application interval of 14 days, and a minimum PHI of 0 days.

- The registrant must propose a higher tolerance for residues of mancozeb in or on papayas. The available data indicate that residues of mancozeb exceeded (up to 12.6 ppm) the established tolerance following treatment at ca. 1x the maximum seasonal application rate allowed by PD 4.

References (used):

MRID(s): 40869709. 40869710.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40869709 and 40869710) submitted data from two tests conducted in HI pertaining to residues of mancozeb and ETU in or on papayas harvested immediately following the last of 13 or 15 applications of the 80% WP formulation at 2 and 2.4 lb ai/A (ca. 1x the maximum single application rate allowed by PD 4). Applications were made

using conventional ground equipment. Results of these tests are detailed below.

PHI (days)	No. of Applns. = rate[a]	Residues (ppm)[b] Mancozeb Range	ETU Range	Commodity (No. of samples)
0	13(2) = 26	10.9-12.6	0.36-0.55	Unwashed WhFrt(2)
		5.1-6.1	0.44-0.49	Washed WhFrt(2)
		4.5-5.0	0.16-0.19	Unwashed Pulp(2)
		1.8-2.1	0.15-0.16	Washed Pulp(2)
0	15(2.4) = 36	5.4-6.4	0.20-0.31	Unwashed WhFrt(2)
		0.55-0.79	0.10-0.14	Washed WhFrt(2)
		0.59-0.77	0.05-0.09	Unwashed Pulp(2)
		<0.05	0.06,0.08	Washed Pulp(2)

[a] Rate in lb ai/A.
[b] Reported residue values for mancozeb and ETU were corrected using average method recovery of 92-94 and 89-118%, respectively.

Apparent residues of mancozeb and ETU were <0.05 ppm (ND) and <0.01(ND)-0.017 ppm, respectively, in or on two samples each of untreated whole fruit and pulp. Mancozeb analyses were conducted using a colorimetric method (Keppel) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries of mancozeb were 92-93% from two samples of fruit and 93% from two samples of pulp each fortified with mancozeb at 0.05-12 ppm. Recoveries of ETU were 88-107% from two samples of fruit and 78-118% from two samples of pulp each fortified with ETU at 0.01-0.5 ppm. Samples were stored for 40-71 days prior to analysis for mancozeb and ETU by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data. Storage stability studies in apples indicate that residues of ETU are stable up to three months in frozen storage.

Geographic representation for papayas is adequate since the test state of HI accounted for virtually all (100%) of the 1988 U.S. papaya production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). The available data indicate that the established tolerance may be too low. Residues of mancozeb exceeded the established tolerance (up to 12.6 ppm) in or on two samples of whole unwashed papayas harvested immediately following treatment at ca. 1x the maximum seasonal application rate allowed by PD 4. Two samples of unwashed pulp from papayas receiving the same treatment contained detectable residues of mancozeb (up to 5.0 ppm). Residues of ETU up to 0.55 ppm were reported. No concurrently conducted storage stability studies were submitted

to support these data. The registrant must propose a higher tolerance for the residues of mancozeb in or on papayas and papaya pulp.

Peanuts

Tolerance(s):

Tolerances of 0.5 ppm and 65 ppm have been established for the residues of the fungicide mancozeb, a coordination product of zinc ion and maneb (manganous ethylene-bisdithiocarbamate) containing 20% manganese, 2.5% zinc, and 77.5% ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate), in or on peanuts and peanut vine hay, respectively [40 CFR §180.176].

Use directions and limitations:

The 62 and 80% WP, 70% and 75% DF, and 32, 37, and 80 FlC formulations are registered for multiple foliar applications to peanuts at 0.7-1.6 lb ai/A/application using ground and aerial equipment. Applications may be made as needed at 10-14 day intervals. The 37% FlC, and 70 and 75% DF formulations are also registered for seed treatments (shelled peanuts) at 0.8-1.6 lb ai/100 lb seed. A 14-day PHI and a restriction against feeding treated vines to livestock have been established. No maximum number of applications per season or maximum seasonal use rate has been established. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

According to the EBDC PD 4, all labels bearing use directions for peanuts must be revised to specify a maximum application rate of 1.6 lb ai/A/application, a maximum of 8 applications or 12.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required additional data reflecting residues in or on peanut nutmeats and vine hay following applications of the WP and D formulations. In addition, the Guidance Document required a processing study.

The earlier peanut residue data discussed in the Residue Chemistry Chapter were inadequate because the treatments did not reflect the registered zero day PHI and information on length and conditions of sample storage were lacking. In a separate report (Rohm and Haas letter of 11/11/86), Rohm and Haas reported the length, but not the conditions of storage. Peanut samples were

stored 45 to 288 days before analysis. The available processing study was inadequate because samples with non-detectable residues were processed and ETU recoveries were unacceptably low.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRIDs 40879711, 41092004 and 41844802) pertaining to residues of mancozeb and ETU in or on peanut nutmeats, vines, hay, and hulls. The available data indicate that residues of mancozeb will not exceed the established tolerances in or on peanut nutmeats and vine hay harvested 14 days following the last of eight applications of the 80% WP formulation at 1x the maximum single application rate allowed by PD 4 and in or on nutmeats following treatment at 5x. No concurrently conducted storage stability studies were submitted to support these data. Residues of mancozeb and ETU in corn storage stability samples were stable for up to six months in frozen storage.

It should be noted that complete sample histories were not provided for all samples in MRID 41844802. Additionally, since peanut hulls are raw agricultural commodities of peanuts, the registrant must propose a tolerance and provide appropriate supporting residue data. The following are required:

- Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 8 applications or 12.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

- The registrant must propose a tolerance for the residues of mancozeb in or on peanut hulls and submit appropriate supporting residue data.

Rohm and Haas also submitted (1988; MRID 40869711) field residue data reflecting application at an exaggerated rate in support of requirements for a peanut processing study. These data indicate that residues of mancozeb were <0.05 ppm (nondetectable) in or on one sample of nutmeats harvested 14 days following eight applications at 5x the maximum single application rate allowed by PD 4. According to information available in Principles of Field Crop Production, 3rd edition (J. Martin, W. Leonard, and D. Stamp), the maximum theoretical concentration factor for peanut processed commodities is 2.5x. The requirement for a peanut processing study is, therefore, waived because nondetectable residues resulted from field tests conducted at a rate greater than the maximum theoretical concentration factor.

References (used):

MRID(s): 40869711. 41092004. 41844802.

Discussion of the data:

The Mancozeb Task Force (1988; MRIDs 40869711 and 41092004) submitted data from three tests conducted in GA pertaining to residues of mancozeb and ETU in or on peanut nutmeats, hulls, and vine hay following applications of the 80% WP formulation using ground equipment. Results of these tests are presented in the table below.

PHI (days)	No. of Applns. = rate[a]	Residues (ppm)[b] Mancozeb Range	ETU Range	Commodity (No. of samples)
14	8(1.6) = 12.8	<0.05	<0.01	Nutmeat(1)
14	8(8) = 64	<0.05	<0.01	Nutmeat(1)
14	8(1.6) = 12.8	<0.05	<0.01	Nutmeat(2)
		1.37-1.45	<0.01	Hay(2)
		0.16-0.18	<0.01	Hull(2)
		0.05	<0.01	Nut + shell(2)

[a] Rate in lb ai/A.
[b] Reported residue values were corrected for average method recovery.

Apparent residues of mancozeb and ETU were <0.05 ppm (ND) and <0.01 ppm (ND), respectively, in or on two untreated samples of nutmeats, and one sample each of hay, and hulls. Mancozeb analyses were conducted using a colorimetric method (Keppel; Rohm and Haas No. TM-1853-1) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Onley) with a limit of detection of 0.01 ppm. Recoveries were 85 and 96% from two samples of nutmeats, 91% from one sample of hulls, and 97% from one sample of hay fortified with mancozeb at 0.05-1 ppm. Recoveries were 104 and 121% from two samples of nutmeats, 81% from one sample of hulls, and 110% from one sample of hay fortified with ETU at 0.01-0.05 ppm. Samples were stored frozen (-10 C) for 408-412 days (MRID 41092004) or 17 days (MRID 40869711) prior to analysis by Enviro-Bio-Tech, Ltd. No concurrently conducted storage stability studies were submitted to support these data.

The Mancozeb Task Force (1990; MRID 41844802) also submitted data from five tests conducted in AL, GA, NC, TX, and VA pertaining to residues of mancozeb and ETU in or on peanuts harvested 14 days following the last of eight foliar applications (seven applications in NC and nine applications in TX) of the 80% WP formulation at 1.6 lb ai/A/application (1x the maximum single application rate allowed by PD 4) using ground equipment.

Residues of mancozeb and its metabolite ETU are presented in the table below.

PHI	No. of Applns. = Rate (lb ai/A)	Residues (ppm)[a] Mancozeb Range	ETU Range	Max. Storage (days)
Nutmeat				
14	7 = 11.2	<0.015(1)	0.006(1)	759
14	8 = 12.8	<0.015-0.017(3)	<0.003-0.006(3)	765
14	9 = 14.4	<0.015(2)	0.005-0.007(2)	715
--	untreated	<0.015(5)	<0.003(5)	765
Vines				
14	7 = 11.2	19.7(1)	0.608(1)	759
14	8 = 12.8	13.1-25.1(2)	0.217-0.296(2)	754
--	untreated	<0.015-1.19(3)	<0.003(3)	759
Hay				
14	8 = 12.8	1.24-9.00(2)	0.052-0.189(2)	765
14	9 = 14.4	18.3(1)	0.789(1)	715
--	untreated	<0.015-0.028(3)	<0.003(3)	765
Hulls				
14	8 = 12.8	3.06(1)	0.037(1)	323
--	untreated	<0.015(1)	<0.003(1)	323

[a] Reported residue values are corrected for average method recovery; the number of samples is given in parentheses.

Mancozeb analyses were conducted using a colorimetric method (PAM Vol II, Method II) with a limit of detection of 0.015 ppm. ETU analyses were conducted using a GLC/FPD method (Onley, JAOAC 54:528-532) with a limit of detection of 0.003 ppm. Samples were stored frozen (-10 C) for 273-765 days prior to analysis by Enviro-Bio-Tech, Ltd. Complete sample histories were not provided for all samples. No concurrently conducted storage stability studies were submitted to support these data. Method recoveries are presented in the following table.

Sample	Fortification (ppm) Mancozeb	ETU	Recovery (%)[a] Mancozeb	ETU
Nutmeat	0.05	0.01	83.6-94.4(2)	83.0-109(2)
	0.1	0.02	88.8-94.4(2)	76.5-88.7(2)
Vines	0.1	0.01	94.5(1)	70.7-75.5(2)
	3	0.025	88.7(1)	94.4(1)
	20	0.05	94.9(1)	115(1)
	24	0.5	91.0(1)	99.8(1)
Hay	0.1	0.01	67.8-89.2(2)	63.0(1)
	1	0.02	91.4(1)	91.0(1)
	20	0.05	96.1(1)	77.0-108(2)
	--	0.5	--	97.8(1)
Hulls	0.1	0.02	83.6(1)	89.1(1)
	4	0.05	96.0(1)	78.6(1)

[a] The number of samples is given in parentheses.

Geographic representation is adequate since the test states of AL(14%), FL(6%), GA(45%), NC(11%), TX(10%), and VA(7%) accounted for ca. 90% of the 1988 U.S. peanut production (Ag. Statistics Board, NASS, USDA, Aug. 1989). The available data indicate that residues of mancozeb will not exceed the established tolerances in or on peanut nutmeats and vine hay harvested 14 days following the last of eight applications of the 80% WP formulation at 1x the maximum single application rate allowed by PD 4 and in or on nutmeats following treatment at 5x. No concurrently conducted storage stability studies were submitted to support these data. However, residues in frozen corn samples were stable for up to six months in frozen storage. It should be noted that complete sample histories were not provided for all samples in MRID 41844802. Since peanut hulls are a raw agricultural commodity, the registrant must propose a tolerance and provide appropriate supporting residue data.

Rohm and Haas submitted (1988; MRID 40869711) field residue data reflecting application at an exaggerated rate in support of requirements for a peanut processing study. These data indicate that residues of mancozeb were <0.05 ppm (nondetectable) in or on one sample of nutmeats harvested 14 days following eight applications at 5x the maximum single application rate allowed by PD 4. According to information available in Principles of Field Crop Production, 3rd edition (J. Martin, W. Leonard, and D. Stamp), the maximum theoretical concentration factor for peanut processed commodities is 2.5x. The requirement for a peanut processing study is, therefore, waived because nondetectable

residues resulted from field tests conducted at a rate greater than the maximum theoretical concentration factor.

The registrant must, however, revise product labels to specify the maximum application rate, maximum number of applications, minimum application interval, and minimum PHI specified in the PD 4. The registrant must also propose a tolerance for the residues of mancozeb in or on peanut hulls.

Crops with Seed or Propagation Stock Treatments Only

Tolerance(s):

No tolerances have been established for residues of mancozeb in or on flax, pineapple, rice, safflower, or sorghum.

Use directions and limitations:

The 80% WP, 32, 37 and 80% FlC, 70 and 75% DF formulations are registered for seed treatment to flax seeds at 0.13-0.36 lb ai/100 lb seed, rice seeds at 0.07-0.22 lb ai/100 lb seeds, safflower seeds at 0.07-0.1 lb ai/100 lb seeds, and sorghum seeds at 0.1-0.25 lb ai/100 lb seeds. The 80% WP, 32 and 37% FlC, and 70 and 75% DF formulations are also registered for dip treatment to pineapple propagation stock at 2.5-2.6 lb ai/10 gal. These use directions were obtained from the EPA Index to Pesticide Chemicals dated 10/30/84, the EPA Site Listing (SP05) dated 9/25/90, and the product labels registered to members of the Mancozeb Task Force.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, required field and processing data depicting mancozeb residues in or on flax, pineapples, rice, safflower, and sorghum harvested at maturity following treatment of the seeds.

In response to the Guidance Document, the Mancozeb Task Force submitted data (MRID 41091801) pertaining to residues of flax, sorghum, and rice plants grown from treated seeds. The Mancozeb Task Force also submitted data (MRID 40869717) pertaining to ^{14}C-residues in or on cotton, rice and sorghum grown from seeds treated with [^{14}C]mancozeb. The available data indicate that uptake and translocation of mancozeb residues occurred in flax, rice, and sorghum grown from seeds treated with mancozeb.

The need for residue and processing data and tolerances for seed treatments will be reevaluated when the nature of the residue in plants is adequately understood.

The following data are required to maintain the dip treatment use of mancozeb on pineapple propagation stock:

- Data depicting mancozeb, ETU, and other residues of concern in or on pineapple fruit and forage grown from propagation stock treated with a representative WP or FlC formulation at 26 lb ai/A (2.6 lb ai/10 gal with 100 gal/A). Samples must be collected at the shortest interval after planting in which they could be used for food or feed purposes. Tests must be conducted in HI(100%) since this state accounted for virtually all (100%) of the 1988 U.S. pineapple production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). When all the required residue data have been submitted, the registrant must propose tolerances for mancozeb residues of concern in or on pineapple fruit and forage grown from propagation stock. Tolerances must be proposed that reflect either the maximum expected residue levels or if no measurable residues are detected, then the limit of detection of the analytical method.

- A processing study depicting the potential for concentration of mancozeb residues of concern in bran and juice processed from pineapples bearing measurable, weathered residues. If residues concentrate/convert in any product, then a feed additive tolerance must be proposed.

References (used):

MRID(s): 40869717. 41091801.

Discussion of the data:

The Mancozeb Task Force (1985; MRID 40869717) submitted data from one test conducted in MS pertaining to ^{14}C-residues in or on cotton, rice, and sorghum grown from seeds treated with [^{14}C]mancozeb. Seeds were treated with radiolabeled 80% WP formulation (specific activity 9.59 mCi/g) at 0.25 ai/100 lb. The specific activity of the mixture of radiolabeled:nonradio-labeled (1:9) mancozeb was 0.959 mCi/g. Subsamples of treated seeds and mature crops samples were radioassayed (combustion followed by LSS). Radioactive residues were 2416 ppm for cotton seeds, 2354 ppm for rice seeds, and 2491 ppm for sorghum seeds prior to planting. No radioactive residues were detected in or on three samples each of cotton seeds, cotton leaves, rice grain, rice leaves, sorghum grain, and sorghum stems and in or on two sorghum leaf samples. Radioactive residues were 0.07-0.09 ppm in or on three samples of rice stems and were 0.0194 ppm in or on one sample of sorghum leaves.

The Mancozeb Task Force (1988; MRID 41091801) submitted data from six tests (two tests for each crop) conducted in PA and MS pertaining to the seed treatment of flax, sorghum and rice. Grain and straw of flax, rice, and sorghum were harvested at maturity (136-168 days) following treatment of the seed with the 80% WP formulation at 4 or 4.5 oz ai/100 lb seed. Residues of mancozeb and ETU, respectively were 2393.9 and 14.3 ppm in or on one sample of flax, 1210 and 8.2 ppm in or on one sample of rice, and 1100 and 3.47 ppm in or on one sample of sorghum seeds prior to planting. Residues of mancozeb in the crop grown from treated seed were: (i) 0.11-0.13 ppm in or on two samples of flax grain; (ii) 0.06 and 0.08 ppm in or on two samples of flax straw; (iii) <0.05 (nondetectable; ND) ppm in or on two samples of rice grain; (iv) 0.11 and 0.15 ppm in or on two samples of rice straw; (v) <0.05(ND)-0.32 ppm in or on four samples of sorghum grain; and (vi) <0.05(ND)-0.12 ppm in or on four samples of sorghum straw. Residues of ETU were: (i) <0.01(ND) ppm in or on two samples each of flax grain and rice grain; (ii) <0.01(ND) and 0.03 ppm in or on two samples of flax straw; (iii) <0.01(ND) ppm in or on two samples of rice grain; (iv) 0.02 and 0.05 in or on two samples of rice straw; (v) <0.01(ND)-0.06 ppm in or on four samples of sorghum grain; and (vi) <0.01(ND)-0.013 ppm in or on four samples of sorghum straw. Apparent residues were nondetectable (<0.05 ppm for mancozeb and <0.01 ppm for ETU) in or on two untreated samples each of flax, rice, and sorghum seed prior to planting, grain, and straw. Reported values for mancozeb (94%) and ETU (89%) were corrected for recovery using 'historical recovery' values. Mancozeb analyses were conducted using a modified colorimetric method (Keppel) with a limit of detection of 0.05 ppm. ETU analyses were conducted using a GLC method (Haines and Alder) with a limit of detection of 0.01 ppm. Samples were stored frozen for 14-82 days prior to analysis for mancozeb and for 25-212 days prior to analysis for ETU. Storage stability data pertaining to wheat grain may be translated to support the data from grain samples in this study; no storage stability data are available to support the data from straw samples. Recovery of mancozeb and ETU from flax, rice and sorghum samples are presented in the following table:

Commodity	Mancozeb Fort. level (ppm)	Mancozeb Recovery (%)	ETU Fort. level (ppm)	ETU Recovery (%)
Flax:				
seed	2400	90.8	5	75
grain	0.05, 0.1	93.4, 90.6	0.01, 0.1	84, 97.2
straw	0.1	94.4	0.01	70.9
Rice:				
seed	1200	89	0.01	67
grain	0.05, 0.1	88, 93.4	0.01, 0.1	78, 89.1
straw	0.1	89	0.2	90
Sorghum:				
seed	1200	87	0.01	84
grain	0.1-0.3	93-104	0.01-0.1	80-93
straw	0.05-0.1	87.9-95	0.02-0.2	71.5-89

The need for tolerances for seed treatments will be reevaluated when the nature of the residue in plants is adequately understood.

MAGNITUDE OF THE RESIDUE IN ANIMALS

Milk and the Fat, Meat, and Meat Byproducts of Cattle, Goats, Hogs, Horses, and Sheep

Tolerance(s):

Tolerance(s) of 0.5 ppm have been established for the residues of mancozeb, a coordination product of zinc ion and maneb (the whole product calculated as zinc ethylenebisdithiocarbamate), in kidney and liver [40 CFR 180.176].

Conclusions:

The Mancozeb Guidance Document, dated 4/87, reserves the need for additional data pending submission and evaluation of adequate storage stability and metabolism data. Presently, data gaps exist concerning the magnitude of the residue in numerous livestock feed items. Upon receipt of the requested animal metabolism, storage stability, field trial, and processing data, the expected dietary intake for beef cattle, dairy cattle, and swine will be calculated, and the need for additional feeding studies will be reevaluated. In addition, the established

tolerances for kidney and liver will be assessed and the need for any additional tolerances will be determined following submission of adequate data.

References (used):

N/A.

Discussion of the data:

N/A.

Eggs and the Fat, Meat, and Meat Byproducts of Poultry

Tolerance(s):

No tolerances have been established for residues of mancozeb in poultry and eggs.

Conclusions:

The Mancozeb Guidance Document, dated 4/87, reserves the need for additional data following receipt of data requested in the registration standard. Presently, data gaps exist concerning the magnitude of the residues in numerous poultry feed items. Upon receipt of the requested metabolism, field trial and processing data, the expected dietary intake for poultry will be calculated and the need for additional feeding studies will be reevaluated.

References (used):

N/A.

Discussion of the data:

N/A.

TOLERANCE REASSESSMENT SUMMARY

Tolerances and interim tolerances for residues of mancozeb in or on raw agricultural commodities are currently calculated as zinc ethylenebisdithiocarbamate [40 CFR §180.183].

It should be noted that data gaps exist for plant and animal metabolism, residue analytical methods, and storage stability. Thus, on receipt of the data requested in these sections, the conclusions stated below regarding the adequacy of the established tolerances are subject to change. Furthermore, since the data requirements for individual commodities are dependent on metabolism data, we recommend that metabolism data be obtained and submitted prior to any required residue data.

According to the EBDC PD 4, only the food/feed uses of mancozeb on apples, asparagus, bananas, barley, corn (field, sweet, and pop), cotton, crabapples/quince, cranberries, cucumbers, fennel, grapes, melons (cantaloupe, casaba, crenshaw, honeydew, and watermelon), oats, onions (dry bulb and green), papayas, peanuts, pears, potatoes, rye, squash (summer), sugar beets, tomatoes, and wheat will be allowed for reregistration; registrants are required to amend their product labels to reflect changes in use patterns specified by the EBDC PD 4 ruling.

Sufficient data are available to ascertain the adequacy of the established tolerance for residues of mancozeb in or on peanut nutmeats and peanut vine hay; the tolerance for peanut vine hay could potentially be reduced to 25 ppm if there are no additional residues of concern and toxicological considerations permitting.

Insufficient data are available to ascertain the adequacy of the established tolerances for residues of mancozeb in or on apples, asparagus, bananas, barley grain, barley straw, corn (sweet, pop, and field), corn forage and fodder, cottonseed, crabapples, cranberries, cucumbers, fennel, grapes, kidney, liver, melons, oat grain, oat straw, onions (dry bulb), peanuts, pears, potatoes, quinces, rye grain, rye straw, squash (summer), sugar beets, sugar beet tops, tomatoes, and wheat grain. In addition, we note that tolerance-exceeding residues were detected on samples of bananas, field corn fodder, papayas, and sugar beet tops treated at ≤1x the maximum seasonal application rate allowed by PD 4. The registrant may have to propose higher tolerances or, alternatively, lower the maximum application rates.

Processing studies are required for field corn, sweet corn, cottonseed, potatoes, rice, sugar beets, and the crops grown from treated seed (flax, pineapples, rice, safflower, and sorghum).

Label revisions as specified by EBDC PD 4 are required.

Higher tolerances must be proposed for papayas and wheat straw. Alternatively, maximum application rates may be lowered.

In view of the actions required by the EBDC PD 4, the following established tolerances for residues of mancozeb in or on crops which are disallowed should be revoked: carrots and celery.

The need for tolerances for seed treatments will be reevaluated when the nature of the residue in plants is adequately understood.

Feed additive tolerances must be proposed for residues of mancozeb, ETU and other residues of concern in dry apple pomace, sweet corn cannery waste, raisin waste, dry grape pomace, grape juice, and potato chips and dehydrated flakes when all the required residue data are submitted. The food additive tolerance for residues of mancozeb on raisins should be revoked.

Upon receipt of adequate residue data, the following data translations may be made to support tolerances: (i) wheat grain data to support tolerances for barley grain, oat grain, and rye grain; (ii) wheat straw data to support tolerances for barley straw, oat straw, and rye straw; (iii) apple data to support the tolerance for crabapples; (iv) pear data to support the tolerance for quinces; and (v) sweet corn grain and forage data to support the tolerances for popcorn grain and forage. In addition, data to support a tolerance proposal for wheat forage may also be translated to support tolerance proposals for barley forage, oat forage, and rye forage.

The following commodity definitions in 40 CFR §180.183 should be changed in keeping with presently accepted commodity definitions: (i) "corn forage and fodder" should be revised to "field corn forage and fodder", "sweet corn forage", and "popcorn forage"; (ii) "peanut vine hay" should be revised to "peanut hay"; and (iii) "kidney" and "liver" should be revised to "kidney of cattle, goats, hogs, horses, and sheep" and "liver of cattle, goats, hogs, horses, and sheep", respectively. We recommend that the phrase "negligible residue" be removed from the tolerance expression for asparagus.

Although inadequate data are available on some crops for which mancozeb is registered, we are recommending that tolerances be changed on an interim basis while additional data are being generated. Many tolerances can be lowered, which will protect the public health. Our recommendations are tabulated below.

Mancozeb Tolerance Recommendations (40 CFR 180.176)

Crop	Tolerance (ppm)
Apples	1
Asparagus	0.1
Bananas	4/1 in pulp
Barley, Oats, Rye, Wheat	1
", flour	2 (FA)
", bran	4 (FA)
", milled fractions	4 (FA)
", forage & straw	50
Corn, field	0.1
Corn, forage & fodder	15
Corn, sweet & pop	1
Cotton	0.5
Crabapples, Quince	1
Cranberries	7
Cucumbers	4
Fennel	7
Grapes	2
Melons	4
Onions, dry bulb	0.5
Papayas	12
Peanuts	0.5
Peanut hay	25
Pears	1
Potatoes	0.5
Squash, summer	4
Sugar beets	1
Sugar beet tops	100
Tomatoes	4
Kidney	0.5
Liver	0.5

Tolerances to be revoked
Carrots
Celery
Raisins (FA)

Harmonization with CODEX

CODEX limits for EBDC fungicides are grouped under dithiocarbamates. Limits for the dithiocarbamates are established for 19 commodities resulting from the use of ferbam, ziram, mancozeb, maneb, and zineb (including nabam plus zinc sulfide) and are currently expressed as ppm Carbon disulfide. Separate limits (Step 7A) are proposed for ETU present at harvest on four commodities (does not include any ETU formed during processing). Harmonization is impractical at the present time.

AGENCY MEMORANDA CITED IN THIS UPDATE

A summary of the subject memoranda and their associated MRID documents is presented below.

CBRS No.: 2654
Subject: Mancozeb on Lettuce, Peppers, and Beans -- Evaluation of Amendment Dated February 20, 1987.
From: M.F. Kovacs, Jr.
To: C.L. Trichilo
Dated: 12/10/87
MRID: 40118201

CBRS No.: 2725
Subject: Mancozeb (014504) Rohm and Haas Response to Registration Standard, letter of 7/2/87 (90 day response), letter of 7/6/87 (Response to Product Chemistry Data Gaps), letter of 7/6/87 (Response to Residue/Metabolism Data Gaps). EPA Reg. No 707-78.
From: S.V. Hummel
To: L. Rossi
Dated: 4/21/88
MRID: 40258301

CBRS No.: 5280
Subject: Mancozeb Revised Dietary Exposure Analysis for Mancozeb and ETU; Residue Data submitted in response to the Mancozeb Registration Standard.
From: S.V. Hummel
To: V. Bael
Dated: 8/17/89
MRID: 41070001

CBTS Nos.: 5557 and 5558
Subject: Metalaxyl and Mancozeb on Grapes -- Evaluation of Amendment Dated June 23, 1989
From: G.F. Otakie
To: R.D. Schmitt
Dated: 12/11/89
MRID: 41150101

CBRS Nos.: 6357, 6358, and 6359
Subject: EBDC/ETU Monitoring Study Method Validation Preliminary Report.
From: S.V. Hummel
To: B. Maranion
Dated: 7/16/90
MRID: 41343101

CBRS Nos.: 6546-8, 6671-3, 6726-8, and 6757-9
Subject: EBDC/ETU Monitoring Study First Interim Report, Supplemental Report to First Interim Report, EBDC/ETU Monitoring Study Second Interim Report, and Supplemental Report to Second Interim Report.
From: S.V. Hummel
To: K. Martin
Dated: 8/13/90
MRIDs: 41383301, 41452201, 41480601, and 41511801.

CBRS No.: 6575
Subject: Mancozeb and ETU on Tomatoes - Washing Study.
From: S.V. Hummel
To: K. Martin
Dated: 10/25/90
MRID: 41443201

CBRS No.: None [CB No. 7155 and HED No. 0-2032]
Subject: EBDC/ETU Monitoring Study Fourth Quarter and Final Report.
From: S.V. Hummel
To: K. Martin
Dated: 12/4/90
MRID: 41643601

CBRS No.: 7499
Subject: EBDCs - Response to Special Review Data Call In Notice of November 7, 1990, EBDC and ETU residues in apples from field trials using proposed new use pattern, EBDC Task Force letter of December 27, 1990.
From: S. V. Hummel
To: K. Martin
Dated: 5/23/91
MRID: 41731801

CBRS No.: None [CB No. 8750; HED No. 2-0140]
Subject: EBDCs - Response to Special Review Data Call In Notice of November 7, 1990, EBDC and ETU residues in apples from field trials using second proposed new use pattern, EBDC/ETU Task Force letters of April 1, 1991 and September 27, 1991.
From: S. V. Hummel
To: K. Martin
Dated: 1/8/92
MRIDs: 41831501 and 42036901

CBRS No.: None [CB Nos. 8439, 8413, 9110, 9115; HED Nos. 1-2086, 1-2099, 2-0830, 2-0832]
Subject: Mancozeb (014540) - Amendment to add uses to label: barley, apples, pears, cucumbers, melons, squash. Addition of maximum seasonal application rates as required by Mancozeb Registration Standard, Deletion of Dust Uses.
From: S. V. Hummel
To: S. Lewis and K. Martin
Dated: 1/22/92
MRID: None

CBRS No.: None [CB Nos. 8571, 8410, 8411, 8992, 8993, 8995, 9097, 9098, 9001; HED Nos. 1-2347, 1-2089, 1-2090, 2-0605, 2-0606, 2-0604, 2-0760, 2-0594]
Subject: Mancozeb (014504) - Amendment to add uses to label: apples, pears, cucumbers, melons, summer squash. Deletion of uses on sugar beets and caprifigs. Addition of maximum seasonal application rates as required by Mancozeb Registration Standard Deletion of dust uses.
From: S. V. Hummel
To: S. Lewis and K. Martin
Dated: 1/28/92
MRID: None

CBRS No.: None [CB Nos. 8536-8, 8441-3; HED Nos. 1-2275-7, 1-2081-3]
Subject: Mancozeb (014504) - Amendment to add uses to label: apples, pears, cucumbers, melons, squash.
From: S. V. Hummel
To: S. Lewis and K. Martin
Dated: 2/3/92
MRID: None

MASTER RECORD IDENTIFICATION NUMBERS

The following references were obtained from a Guideline Sequence Number search conducted on October 19, 1990 for documents on mancozeb. MRID documents containing data which have been reviewed by the Agency are designated in shaded blocks in the following bibliographic listing of Residue Chemistry Citation (used).

Residue Chemistry Citations (used):

00160780 Rohm and Haas Co. (1986) Distribution and identification of radiolabeled mancozeb metabolism in dairy goats: Report No. 31L-86-04.

00160781 Rohm and Haas Co. (1986) Metabolism study of ^{14}C radiolabeled mancozeb in laying hens; Report No. 31L-86-07.

00164510 Reibach, P. (1986) Distribution of Radiolabeled Mancozeb Metabolites and Degradation Products in Wheat Plants: Addendum to Technical Report No. 31L-86-03: Technical Report No. 310-86-54. Unpublished compilation prepared by Rohm and Haas Co. 121 p.

00164879 Schweitzer, M. (1986) Isolation and Characterization of Radiolabeled Mancozeb: Metabolism Tissues of Lactating Dairy Goats: Technical Report No. 310-86-45. Unpublished study prepared by Rohm and Haas Co. 152 p.

00164880 Smith, S. (1986) Addendum to Metabolism Study of[Carbon 14: Radiolabeled Mancozeb in Laying Hens: Technical Report No. 310-86-52. Unpublished study prepared by Rohm and Haas Co. 266 p.

40258301 Satterthwaite, S. (1986) Comparison of Mancozeb and ETU Residue Levels Resulting from Various Methods of Application: Report No. TR-82-21. Unpublished study prepared by Rohm and Haas Co. 39 p.

40764601 Schweitzer, M. (1988) Analysis of Mancozeb and Ethylenethiourea by FDA Pesticide: Rept. No. 34C-88-41. Unpublished study prepared by QC, Inc. 129 p.

40768001 Schweitzer, M. (1988) Commercial Tomato Processing Study with Tomatoes Treated with Mancozeb: Technical Report No. 34C-88-04. Unpublished study prepared by Rohm and Haas Co. in cooperation with Enviro-Bio-Tech, Ltd. 207 p.

40869701 Satterthwaite, S. (1987) Dithane M-45 Residues in Asparagus: Rohm and Haas Analytical Report No. 31A-87-19. Unpublished study prepared by Rohm and Haas in association with Enviro-Bio-Tech, Ltd. 25 p.

40869702 Satterthwaite, S. (1987) Dithane F-45 Fungicide Residues in Asparagus: Report No. 31A-87-68. Unpublished study prepared by Rohm and Haas in association with Enviro-Bio-Tech, Ltd. 49 p.

40869705 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Field Corn: Report No. 34A-68-47. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 43 p.

40869706 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Cranberries: Report No. 34A-88-67. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 36 p.

40869707 Satterthwaite, S. (1988) Dithane Fungicide and ETU Residues in Cucumber: Report No. 34A-88-21. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 52 p.

40869708 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Onion: Report No. 34A-88-59. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 38 p.

40869709 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Papaya: Report No. 34A-88-68. Unpublished study prepared by Enviro-Bio-Tech Ltd. 38 p.

40869710 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Papaya: Report No. 34A-88-56. Unpublished study prepared by Enviro-Bio-Tech Ltd. 41 p.

40869711 Schweitzer, M. (1988) Peanut Process Component Study with Peanuts Treated with Mancozeb--Residue Analytical Results: Report No. 34C-88-06. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 34 p.

40869712 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Sugar beet: Report No. 34A-88-60. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 50 p.

40869713 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Tomatoes: Report No. 34A-88-51. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 39 p.

40869714 Satterthwaite, S. (1986) Mancozeb and ETU Residues in Tomato: Report No. 31A-86-94. Unpublished study prepared by Enviro-Bio-Tech Ltd. 89 p.

40869715 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Wheat: Report No. 34A-88-65. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 39 p.

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40869717 Schweitzer, M. (1987) Treatment of Cotton Seed, Rice Seed, and Sorghum Seed with Radiolabeled Mancozeb--Magnitude of the Residue in Harvested Crops: Report No. 31C-87-35. Unpublished study. 41 p.

40913301 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Potatoes: Rohm and Haas Analytical Report No. 34A-88-52. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 38 p.

40913303 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Bananas: Rohm and Haas Analytical Report No. 34A-88-71. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 44 p.

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40913306 Satterthwaite, S. (1987) Mancozeb and ETU Residues in Pears: Rohm and Haas Analytical Report No. 31A-87-18. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 36 p.

41070001 Schweitzer, M. (1989) Mancozeb and ETU Storage Stability Study on Apple, Tomato, and Wheat-Final Report: Rept. No. 34C-88-56. Unpublished study prepared by Rohm and Haas Co. 150 p.

41091601 Schweitzer, M. (1989) Determination of the Magnitude of the Residue Due to Mancozeb and ETU in Potato Processed Fractions: Laboratory ID: Technical Report 34-89-15. Unpublished study prepared by Enviro-Bio-Tech, Ltd., in cooperation with National Food Laboratory Inc. 165 p.

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41091801 Schweitzer, M. (1989) Determination of the Magnitude of the Residue Due to Mancozeb and ETU in Selected Crops Grown from Seed Treated with Mancozeb: Technical Report 34-89-18. Unpublished study prepared by Rohm and Haas Co. 207 p.

41092001 Satterthwaite, S. (1989) Mancozeb and ETU Residues in Grapes: Project ID: 34A/89/09. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 153 p.

41092002 Satterthwaite, S. (1989) Mancozeb and ETU Residues in Grapes: Report No. 34A-88-81. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 66 p.

41092003 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Onion: Project ID: Report No. 34A-88-76. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 39 p.

41092004 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Peanuts: Project ID: 34A-88-79. Unpublished study prepared by Enviro-Bio-Tech. 44 p.

41092005 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Winter Wheat: Project ID: Report No. 34A-88-85. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 41 p.

41092006 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Cucumbers: Project ID: Report No. 34A-88-78. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 67 p.

41092007 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Apple: Project ID: Report No. 34A-88-77. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 64 p.

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41095201 Mazza, L.; Schweitzer, M. (1989) Mancozeb Metabolism in Tomatoes: Technical Report No. 34-89-19. Unpublished study prepared by Rohm and Haas Co. 289 p.

41150101 Cheung, M. (1989) Metalaxyl Residues in Grapes and Grape Fractions Resulting from Applications of Ridomil MZ58: Project ID ABR-89016. Unpublished study prepared by Ciba-Geigy Corp. 225 p.

41343101 Loftus, M. (1989) Preliminary Report: EBDC/ETU National Food Survey Method Validation Study: Lab Project Number: ETU/89/01. Unpublished study prepared by Morse Laboratories,

Inc. in Association with McKenzie Laboratories, Inc., Craven Laboratories and EN-CAS Analytical Laboratories. 464 p.

41443201 Schweitzer, M. (1989) The Effect of Washing on the Concentration of Mancozeb and ETU on Tomatoes Treated with Mancozeb--Pilot Plant Study: Technical Report 34-89-26; Project ID: RH-01-89: 88-0276. Unpublished study prepared by Rohm and Haas Co., National Food Laboratory and Enviro-Bio-Tech, Ltd. 120 p.

41483801 Satterthwaite, S. (1990) Mancozeb and ETU Residues in Processed Grapes: Rohm and Haas Analytical Report No. 34A-89-26. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 94 p.

41731801 Loftus, M. ; Kovacs, M. (1990) 1990 Mancozeb And Metiram Apple Field Study-Early Season Treatments Through Full Bloom: Lab Project Number: ETU 90-13. Unpublished study prepared by Rohm and Haas Co. 582 p.

41831501 Loftus, M. (1991) 1990 Mancozeb and Metiram Apple Field Study: Lab Project Number: ETU 91-02. Unpublished study prepared by Rohm and Haas Co. 691 p.

41844801 Satterthwaite, S. (1990) Mancozeb and ETU Residues in Tomato: Lab Project Number: 34A-90-20. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 63 p.

41844802 Satterthwaite, S. (1990) Mancozeb and ETU Residues in Peanuts: Lab Project Number: 34A-90-21. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 211 p.

41901102 Pitt, J. (1991) Maneb and Mancozeb and their Metabolite Ethylene Thiourea: Magnitude of the Residue in Tomato: Lab Project Number ML89-0142-PEN: BR-89-23. Unpublished study prepared by Morse Laboratories, Inc. 420 p.

41976101 Haines, L. (1991) Mancozeb and ETU Storage Stability Study on Apples: Lab Project Number: 34-91-45. Unpublished study prepared by Rohm and Haas Co. and Enviro-Bio-Tech, Ltd. 149 p.

42036901 Loftus, M. (1991) 1990 Mancozeb and Metiram Apple Field Study: Storage Stability Study: Lab Project Number: ETU 91-06. Unpublished study prepared by Technical Assessment Systems, Inc. 216 p.

42155901 Satterthwaite, S. (1988) Mancozeb and ETU Residues in Sweet Corn: Lab Project Number: 34A-88-84. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 42 p. 41901102 Pennwalt Corporation. (1988) Analysis of Maneb, Mancozeb, and ETU Residues in Tomato: Unpublished Study prepared by Atochem Study (#BR-89-23) and Morse Laboratories (Project # ML89-0142-PEN). 97 p.

Residue Chemistry Citations (not used)

[The following MRID(s) contain data submitted in response to a Special Review Data-Call-In Notice issued 3/31/88, requiring the registrants of all of the EBDCs to conduct a Market Basket survey. These have been reviewed by the Agency for purposes of dietary exposure and are not useful for purposes of satisfying residue chemistry data requirements for reregistration.]

41343101 Loftus, M. (1989) Preliminary Report: EBDC/ETU National Food Survey Method Validation Study: Lab Project Number: ETU/89/01. Unpublished study prepared by Morse Laboratories, Inc. in Association with McKenzie Laboratories, Inc., Craven Laboratories and EN-CAS Analytical Laboratories. 464 p.

41383301 Slesinski, R. (1990) EBDC/ETU National Food Survey...EBDC Data Call-in Notice of March 10, 1989: First Interim Report: Project No. ETU 89-01. Unpublished study prepared by Technical Assessment Systems, Inc., Morse Laboratories, Inc., Craven Laboratories, Inc. and others. 1804 p.

41452201 Slesinski, R. (1990) EBDC/ETU National Food Survey: Supplemental Report: Project I.D. No. ETU 89-01: Report I.D. No. ETU 90-02. Unpublished study prepared by Technical Assessment Systems, Inc., and others. 164 p.

41474901 Slesinski, R. (1990) EBDC/ETU National Food Survey: Modified Survey Design: Lab Project Number: ETU 90-04. Unpublished study prepared by Technical Assessment Systems, Inc. 79 p.

41480601 Slesinkski, R. (1990) EBDC/ETU National Food Survey: Second Interim Report: Lab Project Number: ETU 89-01: ETU90-03. Unpublished study prepared by Technical Assessment Systems, Inc. 2113 p.

41511801 Slesinski, R. (1990) Supplement to Second Quarter Interim Report: MRID No. 41480601: EBDC/ETU National Food Survey: Lab Project No.: ETU 90-05: ETU 89-01. Unpublished study prepared by Technical Assessment Systems, Inc. 36 p.

41643601 Slesenski, R. (1990) EBDC/ETU National Food Survey: Fourth Quarter and Interim Final Report: Lab Project Number: ETU 89-01: ETU 90-09. Unpublished study prepared by Morse Laboratories, Inc. in association with McKenzie Laboratories, Inc. and EN-CAS Laboratories. 2877 p.

[The following MRID(s) contain data what were previously reviewed in the Mancozeb Residue Chemistry Chapter dated 9/10/86.]

40913302 Satterthwaite, S. (1986) Mancozeb and ETU Residues in Cucumbers: Rohm and Haas Analytical Report No. 31A-86-10. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 87 p.

[The following MRID(s) contain data pertaining to mancozeb uses which are no longer allowed by the EBDC PD 4.]

40869703 Satterthwaite, S. (1986) Supplemental Report Analytical Report of Dithane and ETU for Carrot Residue Samples: Analytical Report No. 31A-86-06. Unpublished study prepared by Rohm and Haas. 4 p.

40869704 Satterthwaite, S.T. (1986) Supplemental Report Analytical Reports of Dithane and ETU for celery samples: Lab. Proj. ID 31A-86-11. Unpublished study prepared by Rohm and Haas Co. 5 p.

41901103 Pitt, J. (1991) Maneb and Mancozeb and their Metabolite Ethylene Thiourea: Magnitude of the Residue in Celery: Lab Project Number ML89-0151-PEN: BR-89-24. Unpublished study prepared by Morse Laboratories, Inc. 284p.

[The following MRID(s) contain data that were either not submitted in response to the Guidance Document or contain data that are not useful in satisfying residue chemistry data requirements for reregistration.]

00164640 Yeh, S. (1986) Mancozeb and ETU Storage Stability Study on Apple, Tomato and Wheat: (Interim Study): Technical Report No. 310-86-148: 310-86-43. Unpublished study prepared by Rohm & Haas, Spring House Research Laboratories. 132 p.

40118201 Fort, T.; Mull, R. (1987) Magnitude of the Residues on Lettuce, Peppers, and Beans After Treatment with Manzate 200 Fungicide: Report No. AMR-773-87. Unpublished study prepared by E. I. du Pont de Nemours & Co., in cooperation with Enviro-Bio-Tech., Ltd. 459 p.

40171117 Gaidano, R. (1986) Benalaxyl: Residues in Cucumbers, Australia. Unpublished study prepared by Montedison. 9 p.

40171121 Gaidano, R. (1986) Benalaxyl: Residues in Potatoes, Italy, New Zealand, U. K., Greece, Federal Rep. Germany (F. R. G.). Unpublished study prepared by Montedison. 67 p.

40380601 Satterthwaite, S. (1987)[Carbon 14: Dithane M-45 Fungicide 30/60 Day Plantback Residue Study: Technical Report No. 31C-87-14. Unpublished study prepared by Rohm and Haas Co. in cooperation with Enviro-Bio-Tech, Ltd. 104 p.

40381917 Chilton Research Services (1977) An Investigation of the Normal Preparation Practices for Fruits and Vegetables Before Eating or Processing: PD 1 Dietary Exposure Rept. #003. Unpublished study. 63 p.

40381918 Petersen, B.; Chaisson, C.; Eickhoff, J. (1987) Anticipated Residues and Chronic Dietary Exposure Analysis for Mancozeb and ETU: PD 1 Dietary Exposure #004. Unpublished study prepared by Technical Assessment Systems. 237 p.

40381919 Han, J. (1977) Stability of [Carbon 14]-ETU and[Carbon 14:-Maneb Residues in Canned Vegetables: PD 1 Dietary Exposure Rept. #005. Unpublished study prepared by E. I. du Pont de Nemours and Co. 21 p.

40381923 Phillips, W.; Grady, M. (1978) A Nationwide Market Basket Survey for Residues of Ethylenebisdithiocarbamates and Ethylenethiourea in Tomatoes and Tomato Products: PD 1 Dietary Exposure Rept. #009. Unpublished study prepared by Technological Resources, Inc. 21 p.

40381924 Phillips, W.; Grady, M.; Gordon, C.; et al. (1982) Table Top Study of Fungicide Residues in Meals prepared in Homes and Restaurants: PD 1 Dietary Exposure Rept. #010. Unpublished study prepared by Technological Resources, Inc. and Rohm and Haas Co. 22 p.

40381929 Johnson, R.; Hafer, J. (1987) ETU Content in Commercial Dithane: Lab. Proj. ID RWN-87-131. Unpublished study prepared by Rohm and Haas Co. 12 p.

40433002 Solomon, H.; Lutz, M. (1987) Mancozeb: Oral (Gavage) Developmental Toxicity Study in Rabbits: [Analytical Report]: Report No. 31A-87-49; 86R-021. Unpublished study prepared by Rohm and Haas Co. 16 p.

GENERIC DATA REQUIREMENTS TABLE

TABLE A. GENERIC DATA REQUIREMENTS FOR MANCOZEB.[1]

Data Requirement[2]	Test Substance[3]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[4]		Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
40 CFR §158.240 Residue Chemistry					
171-2. Chemical Identity[5]					
171-3. Directions for Use[6]		(See Index[7])			
171-4. Nature of the Residue (Metabolism) - Plants	PAIRA	Partially	00152696 00160703 00164510	00156715 00164509 41095201	Yes[8,9]
171-4. Nature of the Residue (Metabolism) - Ruminants	PAIRA & plant metabolites	Partially	00160780	00164880	Yes[10]
- Poultry	PAIRA & plant metabolites	Partially	00160781	00164879	Yes[11]
171-4. Residue Analytical Methods	TGAI & metabolites	Partially	40764601	41343101	Yes[12,13]
171-4. Storage Stability	TEP or PAI & metabolites	Partially	41070001 41976101	41643601	Yes[14,15,16]
171-4. Magnitude of Residue in Plants[17]					
Root and Tuber Vegetables					
- Carrots	TEP	No			No[18]

(Continued, footnotes follow)

TABLE A. (Continued).

Data Requirement	Test Substance[1]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[2]	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
- Potatoes	TEP	Partially	40913301 41091601	Yes[19,20,14]
(processed commodities)	TEP	Partially	41091601	Yes[21,14]
- Sugar beets	TEP	Partially	40869712	Yes[22,14]
(processed commodities)	TEP	Yes	00160708	No
Leaves of Root and Tuber Vegetables				
- Sugar beet tops	TEP	Partially	40869712	Yes[23,24,14]
Bulb Vegetables				
- Onions	TEP	Partially	40869708 41092003	Yes[25,26,14]
Leafy Vegetables (except Brassica)				
- Celery	TEP	No		No[27]
- Fennel	TEP	No		Yes[28,14]
Fruiting Vegetables (Except Cucurbits)				
- Tomatoes	TEP	Partially	40869713 40869714	Yes[29,30,14]
(processed commodities)	TEP	Yes	40768001	No[31]
Cucurbit Vegetables				
- Cucumbers	TEP	Partially	40869707 41092006	Yes[32,33,14]
- Melons	TEP	No		Yes[34,14]
- Pumpkins	TEP	No		Yes[35]

(Continued, footnotes follow)

TABLE A. (Continued).

Data Requirement	Test Substance[1]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[2]	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
- Summer squash	TEP	No		Yes[36,37,14]
Pome Fruits				
- Apples	TEP	Partially	41092007 41731801 41831501 42036901	Yes[38,39,14]
(processed commodities)	TEP	Partially		Yes[40]
- Crabapples	TEP	No		Yes[41]
- Pears	TEP	Partially	40913305 40913306	Yes[42,43,14]
- Quinces	TEP	No		Yes[44]
Small Fruits and Berries				
- Cranberries	TEP	Partially	40869706	Yes[45,46,14]
- Grapes	TEP	Partially	41092001 41092002 41150101	Yes[47,48,14]
(processed commodities)	TEP	Partially	41483801	Yes[49]
Tree Nuts				
- Almonds	TEP	No		Yes[50]
- Walnuts	TEP	No		Yes[51]
Cereal Grains				
- Barley	TEP	No		Yes[52]
(processed commodities)	TEP	No		Yes[53]

(Continued, footnotes follow)

TABLE A. (Continued).

Data Requirement	Test Substance[1]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[2]	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
- Corn, field	TEP	Partially	40869705	Yes[54,55,14]
(processed commodities)	TEP	Partially	41091701	Yes[56,14]
- Corn, sweet & popcorn	TEP	Partially	41093201	Yes[57,58,14]
(processed commodities)	TEP	Partially	41093201	Yes[59,14]
- Oats	TEP	No		Yes[60]
(processed commodities)	TEP	No		Yes[61]
- Rye	TEP	No		Yes[62]
(processed commodities)	TEP	No		Yes[63]
- Wheat	TEP	Partially	40869715 40869716 41092005	Yes[64,65,14]
(processed commodities)	TEP	Yes		No[66]
Forage, Fodder, and Straw of Cereal Grains				
- Barley forage, hay & straw	TEP	No		Yes[67]
- Field corn forage, fodder & silage	TEP	Partially	40869705	Yes[68,69,14]
- Sweet and pop corn forage, fodder & silage	TEP	No		Yes[70,71,14]
- Oat forage, hay, & straw	TEP	No		Yes[72]

(Continued, footnotes follow)

TABLE A. (Continued).

Data Requirement	Test Substance[1]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[2]		Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
- Rye forage & straw	TEP	No			Yes[73]
- Wheat forage, hay, & straw	TEP	Partially	40869715 41092005	4089716	Yes[74,75,76,77,1]
Miscellaneous Commodities					
- Asparagus	TEP	Partially	40869701	40869702	[78,79]
- Bananas	TEP	Partially	40913303	40913304	Yes[80,81,82,14]
- Cottonseed	TEP	No			Yes[83,84,14]
(processed commodities)	TEP	No			Yes[85,14]
- Papayas	TEP	Partially	40869709	40869710	Yes[86,87]
- Peanuts	TEP	Partially	40879711 41844802	41092004	Yes[88,89]
(processed commodities)	TEP	Yes	40869711		No[90]
- Tobacco	TEP	No			Yes[91]
Crops with Seed or Propagation Stock Treatments Only					
- Flax	TEP	Partially	41091801		Reserved[92]
(processed commodities)	TEP	No			Reserved
- Pineapples	TEP	No			Yes[93,14]
(processed commodities)	TEP	No			Yes[94,14]

(Continued, footnotes follow)

TABLE A. (Continued).

Data Requirement	Test Substance[1]	Does EPA have data to satisfy this requirement?	Bibliographic Citation[2]	Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?
- Rice	TEP	Partially	40869717 41091801	Reserved[92]
(processed commodities)	TEP	No		Reserved
- Safflower	TEP	No		Reserved[92]
(processed commodities)	TEP	No		Reserved
- Sorghum	TEP	Partially	40869717 41091801	Reserved[92]
(processed commodities)	TEP	No		Reserved
171-4. Magnitude of residue in Meat/Milk/Poultry/Eggs				
- Meat/Milk (Liver and Kidney)	TGAI or Plant Metabolites	No		Reserved[95]
- Poultry/Eggs	TGAI or Plant Metabolites	No		Reserved[96]

1. The data requirements discussed in this Update Document include only those end-use products registered by the Mancozeb Task Force [Rohm and Haas, Ciba-Geigy, E.I. du Pont, and Atochem (formerly Pennwalt)]. When end-use product DCIs are developed (e.g., at issuance of the RED), RD should require that all end-use product labels (including SLNs) be amended, if necessary, such that they are consistent with the basic producer labels.

2. Outstanding data requirements for which no data have been submitted in response to the Mancozeb Reregistration Standard Guidance Document 4/87 appear in shaded blocks.

(Continued, footnotes follow)

TABLE A. (Continued).

3. Test Substance: PAI = purified active ingredient; PAIRA = purified active ingredient, radiolabeled; TEP = Typical end-use product; TGAI = technical grade of the active ingredient; MP = manufacturing-use product.

4. These references were submitted in response to the Mancozeb Guidance Document dated 4/87 and the 1987 EBDC Special Review Data Call-In-Notice. Underlining designates references that have been reviewed for this Update document.

5. The same chemical identity data are required as under 40 CFR §158.150-190, with emphasis on impurities that could constitute residue problems. Refer to Product Chemistry Data Requirements tables.

6. According to the EBDC PD 4, only the food/feed uses of mancozeb on the following crops will be allowed for reregistration: apples, asparagus, bananas, barley, corn (field, sweet, and pop), cotton, crabapples/quince, cranberries, cucumbers, fennel, grapes, melons (cantaloupe, casaba, crenshaw, honeydew, and watermelon), oats, onions (dry bulb and green), papayas, peanuts, pears, potatoes, rye, squash (summer), sugar beets, tomatoes, and wheat. Registrants are required to amend their product labels to reflect changes in use patterns specified by the EBDC PD 4 ruling.

7. Pertinent product labels registered by the basic producers were used to create this document.

8. The tomato metabolism study (MRID 41095201) submitted in response to the Guidance Document does not delineate the qualitative nature of [^{14}C]mancozeb residue in tomatoes. This study is potentially upgradeable. The registrant must confirm the identifications of metabolites by a second method such as GC or MS. The identity of ca. 60% of the residue characterized as natural products such as lipids, carbohydrates, and amino acids in tomato fruit is considered putative; the incorporation of [^{14}C]mancozeb into natural products must be verified. The registrant must submit information regarding the intervals and conditions of sample storage.

9. After reevaluations of previously submitted plant metabolism studies on soybean, sugar beet, and wheat metabolism studies, it is concluded that the qualitative nature of [^{14}C]mancozeb residue in these crops remains inadequately understood. The following data are required: Data depicting the uptake, distribution, and metabolism of [^{14}C]mancozeb in a pome fruit (apples) and in a grain crop. A completely characterized test substance representative of technical mancozeb used in commercial formulation (including impurities) must be applied under conditions representing normal cropping practices and at rates high enough to permit

TABLE A. (Continued).

characterization of ^{14}C-residues. The identities and quantities of residues in mature plant parts must be determined in order to elucidate terminal residues. Data depicting all terminal residue components in commodities at the time of harvest should be expressed as the percentage of the total recovered radioactivity and concentration (ppm). Confirmation of the identities of residue using a suitable method such as MS or HPLC is also required. Representative samples from these studies must also be analyzed by the residues analytical methods developed for data collection and tolerance enforcement to ascertain that these methods are capable of adequately recovering all metabolites of concern.

10. The qualitative nature of [^{14}C]mancozeb residue in ruminants is not adequately understood. The available study on lactating goats (MRIDs 00160780 and 00164880) is potentially upgradeable. Additional data are required depicting the characterization and identification of residues in fat. The identity of metabolites, other than ETU, in tissues and milk is considered tentative because TLC resolution was poor and no confirmatory procedures were performed. The evidence for the presence of radioactivity in natural products was inconclusive since the levels of ^{14}C-activity in these components was quite variable. Representative samples from these studies must be analyzed by the residue analytical methods developed for data collection and tolerance enforcement to ascertain that these methods are capable of adequately recovering all metabolites of concern.

11. The qualitative nature of [^{14}C]mancozeb residue in poultry is not adequately understood. The available studies on laying hens (MRIDs 00160781 and 00164879) are potentially upgradeable. Additional data are required depicting the characterization and identification of residues in eggs and tissues. Only ca. 30-50% of the TRR in eggs and tissues were characterized. The unanalyzed fractions from ion exchange chromatography and radioactivity at the origin of TLC plates were not sufficiently characterized. The identification of residues is considered tentative due to poor separation of metabolites on TLC or the failure to perform confirmatory analyses. In eggs, the only metabolites with verified identities were ETU (up to 7% of the TRR) and glycine (maximum of 10%; uncertain due to the co-migration of EDA with non-derivatized glycine on TLC). In liver, the presence of ETU was confirmed (<1% of the TRR), as were NAcEDA (1%) and EDA (percentage undetermined due to co-migration of glycine with EDA). Representative samples from these studies must be analyzed by the residues analytical methods developed for data collection and tolerance enforcement to ascertain that these methods are capable of adequately recovering all metabolites of concern.

12. At the present time, analytical methods converting all EBDCs and some metabolites to carbon disulfide will be considered adequate for enforcement, along with a specific method for ETU.

TABLE A. (Continued).

13. If the requested data regarding the nature of the residue in plants and animals reveal additional metabolites of toxicological concern, additional analytical methods for data collection and enforcement may be required.

14. To support the field residue and processing data required in this Update document, storage stability studies must be concurrently conducted (in the same laboratory, under the same conditions, and for the same duration) with the field residue and processing studies. If samples from the field residue and processing studies are analyzed within two weeks of collection, and all fresh samples are frozen within a few hours of collection, and all analyses are completed on the same day on which they were begun (from grinding the sample through the determinative step), then the requirement for concurrent storage stability data may be waived.

15. If cattle and poultry feeding studies are required, then fortified storage stability studies will be required on all animal commodities (i.e. tissues, milk, and eggs) for which residue data are submitted to the Agency. Analyses must be conducted over a time period that includes the time interval that each commodity is held in frozen storage prior to residue analyses.

16. The nature of the residue in plants and animals is not adequately understood. If the requested data on plant and animal metabolism indicate the presence of additional metabolites of toxicological concern, data depicting stability of these residues during storage will be required.

17. Rohm and Haas Company has indicated that it will not support uses for dust (D) formulation (CBRS No. 4015, S. Hummel, dated 9/27/88). No data reflecting the dust formulation will be required, provided all dusts are canceled. Data requirements for crop field trials reflecting D formulations remain outstanding for food/feed use sites for which dust formulations are still registered (potatoes, tomatoes, and cucumbers). Current registrants or other interested parties wishing to retain the use of a D formulation should be informed that additional data must be submitted.

18. The EBDC PD 4 does not allow continued use on carrots. All carrot uses must be deleted from product labels. The following are required: Revised labels deleting carrots from all registered mancozeb products. No additional data are required for carrots, provided use directions for carrots are deleted from all mancozeb labels. If, however, any use on carrots is continued for any reason, then full supporting residue data will be required for the label use pattern.

TABLE A. (Continued).

19. Data on potatoes submitted in response to the Guidance Document do not fulfill the requirements for reregistration because geographical representation of adequate data is lacking. The following additional data are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum or 7 applications or 11.2 lb ai/A/season, a minimum application interval of 5 days, and a minimum PHI of 14 days. A PHI of 3 days is allowed in CT, FL, MA, ME, NH, NY, PA, VT, and WI. Additionally, labels must state that use is recommended within an IPM program, and that vine kill should occur 14 days before harvest.

20. Data depicting mancozeb, ETU, and other residues of concern in or on potatoes harvested 3 days following the last of 7 applications at 1.6 lb ai/A/application at 5-day intervals. Tests must be conducted in CO(6%), ME(6%), OR(6%), WA(18%), and WI(6%); these states along with ID(28%) where data are available accounted for ca. 70% of the 1988 U.S. potato production (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989). Samples must be frozen immediately after harvest and analyzed within two weeks of harvest.

21. Data from potato processing studies submitted in response to the Guidance Document do not satisfy the requirements for this topic because: (i) no data were submitted depicting residues in or on dry peels; (ii) no method recovery data were submitted for mancozeb residues in or on whole raw potatoes and in granules, or for ETU in granules; and (iii) no storage stability data were submitted from the performing laboratory, the National Food Laboratory; the limit of detection used in the processing study was four times higher than the limit of detection previously reported. The following data remain outstanding: Data depicting the potential for concentration of mancozeb, ETU, and other residues of concern in chips, granules, and wet and dry peel from potatoes bearing measurable weathered residues. If residues concentrate/concentrate in processed products, then appropriate food/feed additive tolerance must be proposed.

22. Data on sugar beet roots submitted in response to the Guidance Document, combined with previously submitted data, fulfill the requirements for reregistration. No processing data were submitted; however, the previously submitted data discussed in the Residue Chemistry Chapter are adequate. The following additional data are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

23. Data on sugar beet tops submitted in response to the Guidance Document do not fulfill the requirements for reregistration because test was not conducted according to the maximum use pattern allowed by PD 4, and geographical representation is inadequate. Further, we note that current labels for mancozeb use on sugar

TABLE A. (Continued).

beets prohibit the feeding of treated tops to livestock. The Agency considers the restriction for sugar beet top grazing and feeding to be economically impractical (see memorandum by C. Trichilo dated 5/30/87: Economic Importance of Sugar Beet Grazing in Imperial Valley of CA). However, the Agency will consider retaining the feeding restriction on mancozeb labels. The following additional data are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 7 applications or 11.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

24. Data depicting mancozeb, ETU, and other residues of concern in or on sugar beet tops harvested 14 days following the last of 7 foliar applications of a representative WP formulation at a maximum application rate of 1.6 lb ai/A applied at 7-day intervals. Tests must be conducted in CA(21%), ID(16%), and MI(10%), since these states accounted for ca. 70% of the 1988 U.S. sugar beet production (Ag. Statistics Board, NASS, USDA, Aug. 1989). Alternatively, the feeding restriction may be retained/reinstated on all mancozeb labels.

25. Data on onions submitted in response to the Guidance Document do not satisfy the requirements for reregistration because geographic representation is inadequate. Additional field residue data conducted in major onion-growing states other than NY must be submitted. The following additional data are required: Revised labels specifying a maximum application rate of 2.4 lb ai/A/application, a maximum of 10 applications or 24 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 7 days. Application to exposed bulbs will be prohibited.

26. Data depicting mancozeb, ETU, and other residues of concern in or on dry bulb onions harvested 7 days following the last of 10 foliar applications of a representative WP formulation at a maximum application rate of 2.4 lb ai/A applied at 7-day intervals. Tests must be conducted in CO(11%) and CA(32%); these states along with TX(8%) and NY(6%) where data are available accounted for ca. 70% of the 1988 U.S. onion production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA, June 1989, p. 14). Samples must be frozen immediately after harvest and analyzed within two weeks of collection.

27. The EBDC PD 4 does not allow continued use on celery. All celery uses must be deleted from product labels. The following are required: Revised labels deleting celery from all registered mancozeb products. No additional data are required for celery, provided use directions for celery are deleted from all mancozeb labels. If, however, any use on celery is continued for any reason, then full supporting residue data will be required for the label use pattern.

28. No data have been submitted for this topic. Previously submitted residue data on celery may be translated to fennel. The registrant must amend its product labels and submit residue data to reflect the

TABLE A. (Continued).

uses allowed by PD 4 on fennel. The following are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 8 applications or 12.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days. No additional residue data are required.

29. Data on tomatoes submitted in response to the Guidance Document do not fulfill the requirements for reregistration because no data were submitted reflecting the maximum use pattern allowed by PD 4 for tomatoes grown east of the Mississippi River. The following additional data are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 4 applications or 6.4 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days for tomatoes grown west of the Mississippi River. Revised labels specifying a maximum application rate of 2.4 lb ai/A/application, a maximum of 7 applications or 16.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days east of the Mississippi River.

30. Data depicting mancozeb, ETU, and other residues of concern in or on tomatoes harvested 5 days following the last of seven applications of a representative WP or F1C formulation at 2.4 lb ai/A/application at 7-day intervals. Tests on tomatoes must be conducted in states east of the Mississippi River, where this use pattern is allowed (FL).

31. Although the Guidance Document did not require data, the Mancozeb Task Force submitted additional processing data which indicate that residues of mancozeb did not concentrate in the processed commodities of tomatoes. Apparent degradation to ETU residues occurred in some processed products. No additional processing data are required.

32. Data on cucumbers submitted in response to the Guidance Document do not fulfill the requirements for reregistration because geographic representation is inadequate. The following additional data are required: Revised labels specifying a maximum application rate of 2.4 lb ai/A/application, a maximum of 8 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 5 days.

33. Data depicting mancozeb, ETU, and other residues of concern in or on cucumbers harvested 5 days following the last of 8 foliar applications of a representative WP or F1C formulation at a maximum application rate of 2.4 lb ai/A applied at 7-day intervals. Tests must be conducted in CA (11%) and NC(15%); these states along with TX(8%), OH(6%), and neighboring states of MI(19%) and WI(7%) where data are available accounted for ca. 70% of the 1988 cucumber production (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA Crop Database, June 1989, p. 40).

TABLE A. (Continued).

specify a maximum application rate of 4.8 lb ai/A, a maximum of four applications or 19.2 lb ai per season, an application interval of 7 to 10 days, and a minimum preharvest interval to bloom. For the extended application use pattern, the labels must specify a maximum application rate of 2.4 lb ai/A, a maximum of seven applications or 16.8 lb ai per season, an application interval of 7 to 10 days, and a minimum PHI of 77 days. Additionally, labels must state that use is recommended within an IPM program.

39. Data depicting mancozeb, ETU, and other residues of concern in or on apples reflecting the pre-bloom and extended application use patterns (in separate tests). For prebloom use pattern, apples must be harvested at bloom after the last of 4 applications of a representative WP or FlC formulation at 4.8 lb ai/A/application made at 7-day intervals. For extended application use pattern, apples must be harvested 77 days after the last of 7 applications per season of a representative WP or FlC formulation at 2.4 lb ai/A/application made at 7-day intervals. Tests must be conducted in WA(43%), NY(10%)/PA(6%), MI(9%), and VA(5%)/WV(4%) since these states accounted for 77% of the 1988 U.S. apple production (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989). Grazing of livestock in treated areas must be prohibited. Aerial application is allowed in a minimum spray volume of 10 gal/A.

40. The registrant has not submitted a proposal for a feed additive tolerance for mancozeb residues in dry apple pomace. The following data remain outstanding: An appropriate level for the feed additive tolerance for mancozeb residues in dry apple pomace will be determined when the adequacy of the tolerance for residues in or on apples is assessed, following receipt of the requested field data.

41. Data required for apples and processed products will be translated to satisfy the requirements for crabapples. Label revisions, however, are required such that the use patterns allowed by PD 4 for crabapples are identical to apples.

42. Data on pears submitted in response to the Guidance Document do not fulfill the requirements for reregistration because geographic representation of data reflecting the "extended use pattern" is inadequate, and no data reflecting the "prebloom use pattern" have been submitted. The following additional data are required: Revised labels specifying a maximum prebloom application rate of 4.8 lb ai/A/application, a maximum of 4 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of bloom; and a maximum extended application rate of 16.8 lb ai/A/application, a maximum of 7 applications or 16.8 lb ai/A/season, a minimum application interval of 7 days, and a PHI of 77 days. Grazing of livestock in treated areas must be prohibited. Aerial application is allowed in a minimum spray volume of 10 gal/A.

TABLE A. (Continued).

43. Data depicting mancozeb, ETU, and other residues of concern in or on pears reflecting the pre-bloom and extended application use patterns (in separate tests). For prebloom use pattern, pears must be harvested at bloom after the last of 4 applications of a representative WP or FlC formulation at 4.8 lb ai/A/application made at 7-day intervals. For extended application use pattern, pears must be harvested 77 days after the last of 7 applications per season of a representative WP or FlC formulation at 2.4 lb ai/A/application made at 7-day intervals. Tests must be conducted in CA(35%) and WA(36%) since these states accounted for ca. 70% of the 1988 pear production (Ag. Statistics Board, NASS, USDA, Aug. 1989).

44. Data required for pears will be translated to satisfy requirements for quinces. Label revisions, however, are required such that the use patterns allowed by PD 4 for pears are identical to quinces.

45. Data on cranberries submitted in response to the Guidance Document do not satisfy requirements for reregistration because geographical representation is inadequate. The following additional data are required: Revised labels specifying a maximum application rate of 4.8 lb ai/A/application, a maximum of 3 applications or 14.4 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 30 days.

46. Data depicting mancozeb, ETU, and other residues of concern in or on cranberries harvested 30 days following the last of 3 foliar applications of a representative WP, FlC, or DF formulation at a maximum application rate of 4.8 lb ai/A applied at 7 day intervals. Tests must be conducted in WI(36%) since this state, along with MA(48%), NJ(9%), OR(4%), and WA(3%), where data are available, accounted for ca. 80% of the 1988 U.S. cranberry production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989).

47. Data on grapes submitted in response to the Guidance Document do not satisfy the requirements for reregistration because no data were submitted reflecting treatment at 1x the maximum seasonal application rate allowed by PD 4 east of the Rocky Mountains. The following additional field data are required: Revised labels specifying a maximum application rate of 3.2 lb ai/A/application, a maximum of 6 applications or 19.2 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 66 days for grapes grown east of the Rocky Mountains; and a maximum application rate of 2 lb ai/A/application, a maximum of 3 applications or 6 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 66 days for grapes grown west of the Rocky mountains, except for CA where no application is permitted after bloom.

48. Data depicting mancozeb, ETU, and other residues of concern in or on grapes harvested 66 days following the last of 6 foliar applications of a representative WP, FlC, or DF formulation at maximum application rate of 3.2 lb ai/A applied at 7-day intervals. Tests must be conducted in NY, since this state accounted for

TABLE A. (Continued).

most of the 1988 U.S. production of grapes outside of CA (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

49. Data from a grape processing study indicate that residues of mancozeb concentrated up to 30x in raisin waste but did not concentrate in raisins, wet pomace, dry pomace, or juice. Residues were converted to ETU in juice (90% conversion) and raisin waste (34%). Appropriate food/feed additive tolerances will be determined for the processed products of grapes when the adequacy of the tolerance for residues in or on grapes is assessed, following receipt of the required field data.

50. The EBDC PD 4 does not allow mancozeb use on almonds. The 24(c) use on this crop must be canceled.

51. The EBDC PD 4 does not allow mancozeb use on walnuts. The use on this crop must be canceled.

52. Data required for wheat grain will be translated to satisfy requirements for barley grain. Label revisions, however, are required such that the use patterns allowed by PD 4 for barley are identical to wheat.

53. Processing data required for wheat will be translated to satisfy requirements for barley processed products.

54. Data on field corn grain submitted in response to the Guidance Document do not satisfy the requirements for reregistration because no data were submitted reflecting treatments made at 1x the maximum seasonal application rate or the minimum PHI allowed by PD 4. The following additional data are required: Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, a maximum of 10 applications or 12 lb ai/A/season, and a minimum PHI of 40 days.

55. Data depicting mancozeb, ETU, and other residues of concern in or on field corn grain harvested 40 days following the last of 10 applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A/application. Tests for field corn must be conducted in IA(18%), IL(14%), MN(7%), NE(17%), and OH(5%), since these states, along with the neighboring states of IN(8%), KS(3%), WI(3%), and MI(2%), accounted for 80% of the 1988 corn grain production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989).

56. Data from field corn grain processing studies submitted in response to the Guidance Document do not fulfill the requirements for this topic because the commodities were processed from field corn bearing non-

detectable residues of mancozeb and ETU. In addition, no data were submitted for the wet milled products, crude oil and refined oil, or for grain dust. The following additional data are required: A processing study depicting the potential for concentration of mancozeb, ETU, and other residues of concern in wet milled products (starch, crude oil, and refined oil) and in dry milled products (grits, meal, flour, and crude and refined oils) and grain dust from the processing of field corn bearing measurable, weathered residues. If residues concentrate in any product, then appropriate food/feed additive tolerances must be proposed.

57. Data on sweet corn kernels plus cobs (husks removed) submitted in response to the Guidance Document do not satisfy the requirements for reregistration because geographic representation is inadequate. The required data for sweet corn will be translated to support the tolerance for mancozeb residues in or on popcorn. The following additional data are required: Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, maximum of 15 applications or 18 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days for sweet corn and popcorn grown east of the Mississippi River, AR, and LA; and a maximum of 5 applications or 6 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days for sweet corn and popcorn grown west of the Mississippi River (except AR and LA).

58. Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn harvested 7 days following the last of 15 foliar applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A applied at 4 day intervals. Tests must be conducted in FL(8%), NY(6%), and WI(19%), since these states accounted for most of the 1988 U.S. sweet corn production east of the Mississippi River (Vegetable, 1988 Summary, Ag. Statistics Board, NASS, USDA June 1989, p. 9 & 38).

Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn harvested 7 days following the last of 5 foliar applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A applied at 4 day intervals. Tests must be conducted in OR(11%) and WA(14%), since these states, along with MN(17%), for which data are available, accounted for most of the 1988 U.S. sweet corn production east of the Mississippi River (Vegetable, 1988 Summary, Ag. Statistics Board, NASS, USDA June 1989, p. 9 & 38).

59. Data from sweet corn processing study submitted in response to the Guidance Document indicate that residues of mancozeb concentrate in cannery waste and that residues convert to ETU; however, the potential for concentration and the conversion factor could not be calculated since cannery waste was processed from sweet corn bearing non-detectable residues of mancozeb. The following additional data are required: Data depicting the potential for concentration of mancozeb residues of concern in cannery residue prepared from

TABLE A. (Continued).

corn bearing measurable weathered residues. If residues concentrate/convert in this feed item, then an appropriate feed additive tolerance must be proposed.

60. Data required for wheat grain will be translated to satisfy requirements for oat grain. Label revisions, however, are required such that the use patterns allowed by PD 4 for oats are identical to wheat.

61. Processing data required for wheat will be translated to satisfy requirements for oat processed products.

62. Data required for wheat grain will be translated to satisfy requirements for rye grain. Label revisions, however, are required such that the use patterns allowed by PD 4 for rye are identical to wheat.

63. Processing data required for wheat will be translated to satisfy requirements for rye processed products.

64. Data on wheat grain submitted in response to the Guidance Document do not satisfy the requirements for reregistration because wheat grain samples were not collected at the minimum PHI. The following additional data are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 3 applications or 4.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 26 days.

65. Data depicting mancozeb, ETU, and other residues of concern in or on wheat grain harvested 26 days following the last of three applications of a representative WP, FlC, or DF formulation at 1.6 lb i/A/application at 7-day intervals. Tests must be conducted in CO(4%), IL(4%), KS(18%)/MO(4%)/NE(4%), ND(6%), OK(10%)/TX(5%), and WA(7%)/OR(3%)/ID(4%), since these states accounted for ca. 70% of the 1988 U.S. production of wheat (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

66. The Mancozeb Guidance Document did not require processing studies for wheat based on data reviewed in the Residue Chemistry Chapter dated 9/10/86 indicating that mancozeb residues concentrated 2x in flour, 4x in bran, and 4x in shorts, and that ETU residues were non-detectable (<0.01 ppm) in the processed products. Food/feed additive tolerances have been established for mancozeb residues in wheat bran, flour, and milled feed fractions of wheat.

TABLE A. (Continued).

67. Data required for wheat forage, hay, and straw will be translated to satisfy requirements for barley forage, hay, and straw. Label revisions, however, are required such that the use patterns allowed by PD 4 for barley are identical to wheat.

68. Data on field corn fodder submitted in response to the Guidance Document indicate that the established tolerance for corn fodder may be too low. Residues exceeded the established tolerance (up to 12.6 ppm) in or on samples of field corn fodder harvested 54 days following treatment at 0.7x the maximum seasonal application rate allowed by PD 4. Residues of ETU were <0.01(ND) and 0.08 ppm in or on these same samples. The submitted data do not satisfy the requirements for reregistration for the following reasons: (i) no data were submitted reflecting treatment at the maximum seasonal application rate and minimum PHI allowed by PD 4; (ii) no data were submitted depicting residues in or on corn forage; and (iii) geographic representation is inadequate. No concurrently conducted storage stability studies were submitted to support these data. The registrant may have to propose a higher tolerance for residues of mancozeb in or on field corn fodder, upon receipt of appropriate residue data. The following additional data are required: Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, a maximum of 10 applications or 12 lb ai/A/season, and a minimum PHI of 40 days.

69. Data depicting mancozeb, ETU, and other residues of concern in or on field corn forage and fodder harvested 40 days following the last of ten applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A/application. Tests must be conducted in IL(14%), IN(8%), IA(18%), MN(7%), NE(17%), and OH(5%) since these states, along with the neighboring states of KS, SD, WI, and MN, accounted for ca. 70% of the 1988 U.S. production of field corn (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

70. No data have been submitted pertaining to residues of mancozeb and ETU in or on sweet corn forage. Currently, the Agency does not consider feeding restrictions to be practical for sweet corn forage. However, in FL where sweet corn is under grower control, a feeding restriction on sweet corn forage is considered enforceable. The following requirements remain outstanding: Revised labels specifying a maximum application rate of 1.2 lb ai/A/application, maximum of 15 applications or 18 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days for sweet corn and popcorn grown east of the Mississippi River, and in AR and LA; and a maximum of 5 applications or 6 lb ai/A/season, a minimum application interval of 4 days, and a minimum PHI of 7 days for sweet corn and popcorn grown west of the Mississippi River (except AR and LA).

71. Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn and popcorn forage harvested 7 days following the last of 15 foliar applications of a representative WP, FlC, or DF formulation

at 1.2 lb ai/A/application applied at 4 day intervals. Tests must be conducted in FL(8%), NY(6%), and WI(19%) since these states accounted for most of the 1988 U.S. production of sweet corn east of the Mississippi River (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

Data depicting mancozeb, ETU, and other residues of concern in or on sweet corn and popcorn forage harvested 7 days following the last of 5 foliar applications of a representative WP, FlC, or DF formulation at 1.2 lb ai/A/application applied at 4 day intervals. Tests must be conducted in CA(3%), MN(17%), and WA(14%), since these states accounted for most of the 1988 U.S. production of sweet corn west of the Mississippi River (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

72. Data required for wheat forage, hay, and straw will be translated to satisfy requirements for oat forage, hay, and straw. Label revisions, however, are required such that the use patterns allowed by PD 4 for oats are identical to wheat.

73. Data required for wheat forage, hay, and straw will be translated to satisfy requirements for rye forage and straw. Label revisions, however, are required such that the use patterns allowed by PD 4 for rye are identical to wheat.

74. Data on wheat straw submitted in response to the Guidance Document indicate that the established tolerance may be too low. Residues exceeded the tolerance (up to 122 ppm) in or on samples of wheat straw harvested 25 days following treatment at 1x the maximum seasonal application rate allowed by PD 4. Residues of ETU up to 0.13 ppm were reported. No concurrently conducted storage stability studies were submitted to support these data. The registrant must propose a higher tolerance for residues of mancozeb in or on wheat straw. No data pertaining to residues in wheat forage were submitted. The following are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 3 applications or 4.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 26 days. The label also must specify a 26-day pregrazing interval, and that treated seed may not be used for food or feed.

75. The registrant must propose a higher tolerance for residues of mancozeb in or on wheat straw. The available data indicate residues exceeded the tolerance (up to 122 ppm) application at 1x the maximum seasonal application rate allowed by PD 4.

76. Data depicting mancozeb, ETU, and other residues of concern in or on wheat straw harvested 26 days following the last of three applications of a representative WP, FlC, or DF formulation at 1.6 lb i/A/application at 7-day intervals. Tests must be conducted in CO(4%), IL(4%), KS(18%)/MO(4%)/NE(4%),

TABLE A. (Continued).

ND(6%), OK(10%)/TX(5%), and WA(7%)/OR(3%)/ID(4%), since these states accounted for ca. 70% of the 1988 U.S. production of wheat (Agricultural Statistics Board, NASS, USDA Crop Database, Aug. 1989).

77. The registrant must propose a tolerance for residues of mancozeb in or on wheat forage and submit supporting residue data.

78. Data on asparagus submitted in response to the Guidance Document do not satisfy the requirements for reregistration because geographic representation was inadequate and the samples were not collected at the minimum PHI specified in PD 4. The following additional data are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 4 applications or 6.4 lb ai/A/season, a minimum application interval of 10 days, and a minimum PHI of 180 days; 120 days in AZ and CA.

79. Data depicting mancozeb, ETU, and other residues of concern in or on asparagus harvested 180 days following the last of 4 foliar applications of a representative WP, FlC, or DF formulation at a maximum application rate of 1.6 lb ai/A applied at 10 day intervals. Tests must be conducted in WA(37%); this state along with CA(48%), where data are available, accounted for ca. 80% of the 1988 U.S. production of asparagus (Vegetables, 1988 Summary, Ag. Statistics Board, NASS, USDA, June 1989, p.18). Samples must be frozen immediately after collection and analyzed within six months of harvest.

80. Data on bananas submitted in response to the Guidance Document indicate that the established tolerance may be too low. Residues exceeded (up to 1.16 ppm) the tolerance in or on banana pulp after the peel is removed following treatment at ca. 1x and 1.5x the maximum seasonal application rate allowed by PD 4. Residues of ETU were non-detectable (<0.01 ppm) in or on these same samples. The following additional data are required: Revised labels specifying a maximum application rate of 2.4 lb ai/A/application, a maximum of 10 applications or 24 lb ai/A/season, a minimum application interval of 14 days, and a minimum PHI of 0 days.

81. The registrant must propose a higher tolerance for residues of mancozeb in or on bananas, supported by appropriate residue data.

82. The registrant must adequately explain the presence of detectable mancozeb residues in or on untreated controls reported in MRID 40913304.

TABLE A. (Continued).

83. No data have been submitted for this topic. The following additional data are required. Revised labels for cotton grown in the Southwestern U.S. specifying a maximum application rate of 1.6 lb ai/A/application and a maximum of 4 applications or 6.4 lb ai/A/season. Mancozeb may not be applied after the bolls open. The label must specify a numerical PHI consistent with boll opening.

84. Data depicting mancozeb, ETU, and other residues of concern in or on cottonseed harvested after the bolls open following the last of four foliar applications of a representative WP or FlC formulation at 1.6 lb ai/A. Tests must be conducted in the Southwestern U.S. where mancozeb use is allowed (TX and CA).

85. No data have been submitted for this topic. A processing study depicting the potential for concentration of mancozeb, ETU, and other residues of concern in meal, hulls, soapstock, crude oil, and refined oil processed from cottonseed bearing measurable, weathered residues. If residues concentrate/convert in any product, then an appropriate food/feed additive tolerance must be proposed.

86. Data on papayas submitted in response to the Guidance Document indicate that the established tolerance may be too low. Residues of mancozeb exceeded (up to 12.6 ppm) the established tolerance in or on samples of whole unwashed papayas harvested immediately following treatment at ca. 1x the maximum seasonal application rate allowed by PD 4. Residues of ETU up to 0.55 ppm were reported. The following are required: Revised labels specifying a maximum application rate of 2 lb ai/A/application, a maximum of 14 applications or 28 lb ai/A/season, a minimum application interval of 14 days, and a minimum PHI of 0 days.

87. The registrant must propose a higher tolerance for residues of mancozeb in or on papayas and papaya pulp.

88. Data on peanuts submitted in response to the Guidance Document indicate that residues of mancozeb will not exceed the established tolerances in or on peanut nutmeats and vine hay harvested 14 days following the last of eight applications of the 80% WP formulation at 1x the maximum single application rate allowed by PD 4 and in or on nutmeats following treatment at 5x. No concurrently conducted storage stability studies were submitted to support these data. The following are required: Revised labels specifying a maximum application rate of 1.6 lb ai/A/application, a maximum of 8 applications or 12.8 lb ai/A/season, a minimum application interval of 7 days, and a minimum PHI of 14 days.

89. The registrant must propose a tolerance for the residues of mancozeb in or on peanut hulls and submit appropriate supporting residue data.

TABLE A. (Continued).

90. Field residue data conducted at an exaggerated rate study indicate that residues of mancozeb were <0.05 ppm (non-detectable) in or on sample of nutmeats harvested 14 days following eight applications at 5x the maximum single application rate allowed by PD 4. According to information available in Principles of Field Crop Production, 3rd edition (J. Martin, W. Leonard, and D. Stamp), the maximum theoretical concentration factor for peanut processed commodities is 2.5x. The requirement for a peanut processing study is, therefore, waived because non-detectable residues resulted from field tests conducted at a rate greater than the maximum theoretical concentration factor.

91. No data have been submitted for this topic. Data depicting mancozeb, ETU, and other residues of concern in or on green, freshly harvested tobacco receiving multiple foliar applications of the WP or FlC formulations to plant bed and in the field at the maximum registered rate. The registrant must propose a maximum seasonal application rate or a maximum number of application per season. Tests must be conducted in KY(26%), GA(6%), and NC(40%) which accounted for ca. 70% of the 1988 U.S. tobacco production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). If residues in or on dried or cured tobacco exceed 0.1 ppm, a pyrolysis study depicting products derived from the active ingredient is required. Identification of the significant components of the residue must be achieved using [^{14}C]mancozeb.

92. The need for residue and processing data and tolerances to cover seed treatments of mancozeb will be reevaluated when the nature of the residue is adequately understood.

93. No data have been submitted for this topic. The following additional data are required to maintain the dip treatment use of mancozeb on pineapple propagation stock: Data depicting mancozeb, ETU, and other residues of concern in or on pineapple fruit and forage grown from propagation stock treated with a representative WP or FlC formulation at 26 lb ai/A (2.6 lb ai/10 gal with 100 gal/A). Samples must be collected at the shortest interval after planting in which they could be used for food or feed purposes. Tests must be conducted in HI(100%) since this state accounted for virtually all (100%) of the 1988 U.S. pineapple production (Ag. Statistics Board, NASS, USDA Crop Database, Aug. 1989). When all the required residue data have been submitted, the registrant must propose tolerances for mancozeb residues of concern in or on pineapple fruit and forage grown from propagation stock. Tolerances must be proposed that reflect either the maximum expected residue levels or if no measurable residues are detected, then the limit of detection of the analytical method.

94. No data have been submitted for this topic. A processing study is required, depicting the potential for concentration of mancozeb residues of concern in bran and juice processed from pineapples bearing

TABLE A. (Continued).

measurable, weathered residues. If residues concentrate/convert in any product, a feed additive tolerance must be proposed.

95. Upon receipt of the data requested in this Update, the established tolerances for liver and kidney will be reassessed, and the adequacy of the available data regarding the magnitude of residues will be determined with consideration for any additional metabolites of toxicological concern.

96. Upon receipt of the data requested in this Update, the available data for poultry and eggs will be evaluated, with consideration for any additional metabolites of toxicological concern.

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MANCOZEB

REGISTRATION STANDARD UPDATE

PRODUCT CHEMISTRY

TASK 4

(Final Report)

CONFIDENTIAL APPENDICES

Appendix A: 2 Page(s)
Appendix B 1 Page(s)

Confidential Appendices to the Scientific Review of the Registration Standard Update Report for the pesticide mancozeb by the Dietary Exposure Branch [Confidential FIFRA Trade Secret/CBI].

Pages 2-5 of the confidential appendix are not included