DYNAMAC
CORPORATION

PENDIMETHALIN

Task 1: Product Chemistry Chapter

Contract No. 68-01-6670

Final Report

May 10, 1984

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

SUBMITTED BY:

Dynamac Corporation
Enviro Control Division
The Dynamac Bldg.
11140 Rockville Pike
Rockville, MD 20852

PENDIMETHALIN

PRODUCT CHEMISTRY

TASK 1

Introduction

FIFRA 3(c)(2)(A) required the Agency to establish guidelines for registering pesticides in the United States. The Agency requires registrants to provide quantitative data on all added ingredients, active and inert, which are equal to or greater than 0.1% of the product weight.

To establish the composition of products proposed for registration, the Agency requires data and information no only on the manufacturing and formulation processes, but also a discussion on the formation of manufacturing impurities and other product ingredients, intentional and unintentional. Further, to assure that the composition of the product as marketed will not vary from the composition evaluated at the time of registration, applicants are required to submit a statement certifying upper and lower composition limits for the added ingredients, and upper limits only for some unintentional ingredients. Guidelines Subpart B, Subdivision D (47 FR 53208) suggests specific precision limits for ingredients based on the variability of the ingredient as a function of the manufacturing process.

In addition to the data on product composition, the agency also requires data to establish the physical and chemical properties of both the pesticide active ingredient and its formulations. For example, data are needed concerning the identity and physical state of the active ingredient (e.g., melting and boiling point data, ambient vapor pressure and solubility).

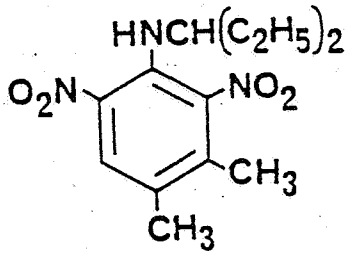
Corresponding to each of the Topical Discussions listed below is the Guidelines Registration No. in "Pesticide Registration; Proposed Data Requirements" of Nov. 24, 1982 (47 FR, No. 227, 53208), which explains the minimum data the Agency will need to adequately assess the product chemistry of pendimethalin.

	Guidelines Reference No. of 40 CFR 158.120
Product Identity and Composition	61-(1-3)
Analysis and Certification of Product Ingredients	62-(1-3)
Physical and Chemical Characteristics	63-(1-21)

PRODUCT IDENTITY AND COMPOSITION

61-1. Product Identity and Disclosure of Ingredients

Pendimethalin is the ANSI approved common name for a herbicide manufactured by American Cyanamid Co.



The che mical name for pendimethalin is N-(1-ethylpropyl)-3,4-dimethyl-2,5-dinitrobenzenamine. Other names include Prowl, Herbadox, Stomp, and AC 92553. Other identifying characteristics and codes are:

Empirical Formula:	$C_{13}H_{19}N_3O_4$
Molecular Weight:	281.3
Shaughnessy No.:	108501

No additional information is required for this topic.

61.2 Description of Beginning Materials and Manufactuing Process

Refer to Confidential Appendix A for a description of the manufacturing process used by the American Cyanamid Co. for 90% technical pendimethalin (EPA Reg. No. 241-245).

The following additional data are required:

- The name and address of the manufacturer or producer of each starting material used for the 90% technical product.

61-3. Discussion of the Formation of Impurities

This topic was not addressed for the 90% technical product; the following is required:

- A discussion of each impurity believed to be present at >0.1% based on knowledge of the beginning materials, all possible chemical reactions, and any contamination.

ANALYSIS AND CERTIFICATION OF PRODUCT INGREDIENTS

62-1. Preliminary Analysis

Refer to Confidential Appendix B for analyses of technical pendimethalin for N-nitroso-pendimethalin. In order to satisfy this data requirement, five or more representative samples should be analyzed for the amount of active ingredient and each impurity present for which a certified limit is required.

- The lack of this information (other than N-nitroso-pendimethalin) for the 90% technical represents a data gap.

62-2. Certification of Ingredient Limits

Refer to Confidential Appendix C for the disclosure of ingredients. Since the data are incomplete, the following data are required:

- A Confidential Statement of Formula was not found in the registration jacket; a recent CSF should be submitted and reviewed. Data in Appendix C was taken from a company data sheet.

62-3. Analytical Methods to Verify Certified Limits

Amercian Cyanamid Co. (The Name, Chemical Identity and Composition of Prowl Herbicide, MRID 00106751; and Recommended Method of Analysis Method M-855.3 dated 6/16/80, MRID 00046347) has submitted a method for the analysis of parent compound and one method to detect two impurities in pendimethalin technical. The first method uses a gas-liquid chromatograph with a flame ionization detector. The second method uses HPLC with a TEA detector (UV detection at 254 nm is used to confirm results). 2-Amino-1-nitronaphthalene is used as an internal standard. These methods are considered adequate for regulatory purposes.

Since the above methods determine only the parent and three impurities, the following is required:

- Quantitative methods to determine the remaining impurities in the technical product.

(The identification of impurities in the technical material is CBI. please see Confidential Appendix A.)

PHYSICAL AND CHEMICAL CHARACTERISTICS

Note that the Residue Chemistry Branch will no longer address the physical/chemical properties of manufacturing-use products (MUPs; here referred to as FIs). These will be considered later by the Registration Division as manufacturers respond to the "data call-in" program. RCB will, however, still consider physical/chemical properties of technical grades of the active ingredient.

Summarized below are several physicochemical properties for 90% technical pendimethalin, EPA Reg. No. 247-245, from a data sheet located in the registration jacket for this product and dated 10/17/74.

63-2. Color: Orange-yellow.
63-3. Physical state: Crystalline.
63-4. Odor: Fruit-like.
63-5. Melting Point: 56-57 C.
63-6. Boiling Point: 330 C.
63-7. Specific gravity: 1.19 at 25 C.
63-8. Solubility: <0.5 ppm in water at 20 C; soluble in chlorinated hydrocarbon and aromatic solvents.
63-9. Vapor pressure: 3.0×10^{-5} mm Hg at 25 C.
63-13 Stability: Stable to alkaline and acidic conditions.

Any properties required by the "Proposed Data Guidelines" (47 FR, No. 227, 53208) and not reported, areregarded data gaps.

Solubility: Data must be provided for solvents in PPM at 20 C; this represents a data gap.

Stability: This is a data gap. The information on stability shall include consideration and discussion of the sensitivity of the active ingredient to metal ions and metal, the stability of the active ingredient at normal and elevated temperatures, and the sensitivity of the active ingredient to sunlight.

8

References:

American Cyanamid Co. 1974. The Name, Chemical Identity and Composition of Prowl Herbicide. Compilation; unpublished study received on unknown data under 5G1567; CDL:094283-A (MRID 00106751).

American Cyanamid Co. 1974. Data sheet received 10/17/74 on physicochemical properties for EPA Reg. No. 241-245 and located in the registration jacket.

American Cyanamid Co. 1980. Data from "Attachments I and III" in correspondence sent to EPA on EPA Reg. No. 241-243, dated 8/27/80 and received 8/28/80. EPA Acesssion No. 243179.

Bliznick, A. 1977. Letter sent to R. Taylor dated Mar 30, 1977: Prowl Herbicide. Unpublished study received Mar 30, 1977 under 241-245; submitted by American Cyanamid Co., Princeton, NJ; CDL:096052-A (MRID 00106788).

King, P.G.; Baker, R. 1980. Recommended Method of Analysis. Method M-855.3 dated Jun 16, 1980. Unpublished study received Sep 24, 1980 under 241-243; submitted by American Cyanamid Co., Princeton, NJ; CDL:243330-A (MRID 00046347).

TABLE A
GENERIC DATA REQUIREMENTS FOR PENDIMETHALIN, EPA REG. NO. 241-245 (90%T)[a]

Data Requirement	Composition[b]	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)?[c]
158.120 Product Chemistry				
Product Identity and Composition:				
61-1 - Product Identity and Disclosure of Ingredients	TGAI	Yes	Refer to Product Chemistry Chapter	No
61-2 - Description of Beginning Materials and Manufacturing Process	TGAI	Partially		Yes
61-3 - Discussion of Formation of Impurities	TGAI	No		Yes
Analysis and Certification of Product Ingredients				
62-1 - Preliminary Analysis of Product Samples	TGAI	Partially		Yes
Physical and Chemical Characteristics				
63-2 - Color	TGAI	Yes		No
63-3 - Physical State	TGAI	Yes		No
63-4 - Odor	TGAI	Yes		No
63-5 - Melting Point	TGAI	Yes		No
63-6 - Boiling Point	TGAI	Yes		No
63-7 - Density, Bulk Density, or Specific Gravity	TGAI	Yes		No

[a]The 90% technical (T) also serves as a manufacturing-use product.
[b]Composition: TGAI = technical grade of the active ingredient; PAI = pure active ingredient.
[c]Data must be submitted no later than 6-8 months from the data of this Standard.

TABLE A
GENERIC DATA REQUIREMENTS FOR PENDIMETHALIN, EPA REG. NO. 241-245 (90% T)[a]

Data Requirement	Composition[b]	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)?[c]
158.120 Product Chemistry (continued)				
63-8 - Solubility	TGAI or PAI	Partially	Refer to Product	Yes
63-9 - Vapor Pressure	PAI	Yes	Chemistry Chapter	No
63-10 - Dissociation Constant	PAI	No		Yes
63-11 - Octanol/Water Partition Coefficient	PAI	No		Yes
63-12 - pH	TGAI	No		Yes
63-13 - Stability	TGAI	Partially		Yes
Other Requirements:				
64-1 - Submittal of samples	N/A	N/A		No

[a]The 90% technical (T) also serves as a manufacturing-use product.
[b]Composition: TGAI = technical grade of the active ingredient; PAI = pure active ingredient.
[c]Data must be submitted no later than 6-8 months from the date of this Standard.

TABLE B
PRODUCT SPECIFIC DATA REQUIREMENTS FOR MANUFACTURING-USE PRODUCTS CONTAINING PENDIMETHALIN, EPA REG. NO. 241-245 (90% T)[a]

Data Requirement	Composition[a]	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted Under FIFRA Section 3(c)(2)(B)?[c]
158.120 Product Chemistry				
Product Identity and Composition:				
61-1 - Product Identity and Disclosure of Ingredients	MP	Yes	Refer to Product Chemistry Chapter	No
61-2 - Description of Beginning Materials and Manufacturing Process	MP	Partially		Yes
61-3 - Discussion of Formation of Impurities	MP	No		Yes
Analysis and Certification of Product Ingredients				
62-1 - Preliminary Analysis of Product Samples	MP	Partially		Yes
62-2 - Certification of Ingredient Limits	MP	Partially		Yes
62-3 - Analytical Methods to Verify Certified Limits	MP	Partially		Yes
Physical and Chemical Characteristics				
63-2 - Color	MP	Yes		No
63-3 - Physical State	MP	Yes		No
63-4 - Odor	MP	Yes		No
63-7 - Density, Bulk Density, or Specific Gravity	MP	Yes		No

[a] The 90% technical (T) also serves as a manufacturing-use product.
[b] Composition: MP = Manufacturing-use product.
[c] Data must be submitted no later than 6-8 months from the date of this Standard.

TABLE B
PRODUCT SPECIFIC DATA REQUIREMENTS FOR MANUFACTURING-USE PRODUCTS CONTAINING PENDIMETHALIN,
EPA REG. No. 241-245 (90% T)[a]

Data Requirement	Composition[a]	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)?[c]
158.120 Product Chemistry (continued)				
63-12 - pH	MP	No	Refer to Product	Yes
63-14 - Oxidizing or Reducing Action	MP	No	Chemistry Chapter	Yes
63-15 - Flammability	MP	No		Yes
63-16 - Explodability	MP	No		Yes
63-17 - Storage Stability	MP	No		Yes
63-18 - Viscosity	MP	No		Yes
63-19 - Miscibility	MP	No		Yes
Other Requirements:				
64-1 - Submittal of samples	N/A	N/A		N/A

[a]The 90% technical (T) also serves as a manufacturing-use product.
[b]Composition: MP=Manufacturing-use product.
[c]Data must be submitted no later than 6-8 months from the date of this Standard.

PENDIMETHALIN

PRODUCT CHEMISTRY

Task 1

(Final Report)

CONFIDENTIAL

CONFIDENTIAL APPENDIXES

Appendix A: 2 pages

Appendix B: 1 page

Appendix C: 2 pages

RIN 2190-95

PENDIMETHALIN REVIEW

Page____ is not included in this copy.

Pages 15 through 19 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

✓ Description of the product manufacturing process.

✓ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

____ FIFRA registration data.

____ The document is a duplicate of page(s) _____.

____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DYNAMAC
CORPORATION

PENDIMETHALIN

Task 2: Residue Chemistry Chapter

Contract No. 68-01-6670

Final Report

May 10, 1984

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

SUBMITTED BY:

Dynamac Corporation
Enviro Control Division
The Dynamac Bldg.
11140 Rockville Pike
Rockville, MD 20852

PENDIMETHALIN

RESIDUE CHEMISTRY

TASK 2

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PENDIMETHALIN

RESIDUE CHEMISTRY

Task 2

INTRODUCTION

Pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] is an herbicide and plant growth regulator registered for use on cotton, field corn, peanuts, potatoes, rice, sorghum, soybeans, sunflowers, and tobacco. The following formulations are registered for use on food/feed crops or tobacco: 60% dispersible granule (DG), 3 and 4 lb/gal emulsifiable concentrate (EC), and 10% granular (G; used on field corn only). All of the above formulations contain pendimethalin as the sole active ingredient although one 3 lb/gal EC (EPA Reg. No. 241-247) is formulated with xylene (used on tobacco only). Applications are made preplant (incorporated), preemergence (may or may not be incorporated), early postemergence (not incorporated), postemergence (incorporated), or foliar (sprayed down tobacco stems for sucker control). Tank mixes with other herbicides are common. Applications may be made with either aerial or ground equipment to all crops except sorghum and tobacco, on which only ground equipment may be used. According to the Preliminary Quantitative Usage Analysis of Pendimethalin (Linda K. Vlier, February 1983, BUD, OPP, EPA), 52% of the domestically available pendimethalin is used on soybeans, 40% on cotton, 8% on corn, and <1% on both sorghum and peanuts. Current usage on peanuts, potatoes, sorghum, and sunflowers is sketchy since registrations were awarded in 1980 and 1981. Specific details on imports and exports of pendimethalin are not available although it is known that pendimethalin is exported. Tolerances are currently expressed in terms of combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite [40 CFR 180.361 (a)] in or on all commodities except peanut hulls. The peanut hull tolerance is currently expressed in terms of combined residues of pendimethalin, its 3,5-dinitrobenzyl alcohol metabolite, and its 2,4-dinitrobenzyl alcohol metabolite [40 CFR 180.361 (b)].

NATURE OF THE RESIDUE IN PLANTS

Conclusions:

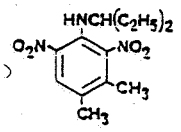
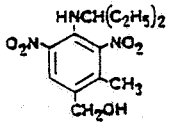
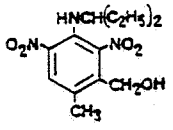
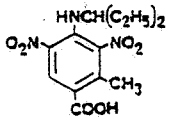
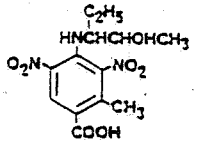
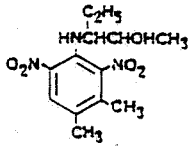
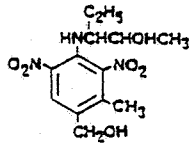
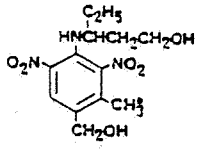
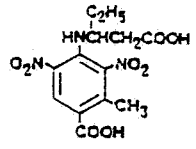
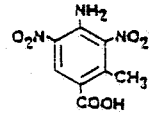
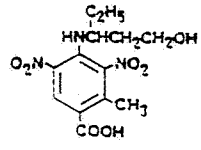
The metabolism of pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] is not adequately understood due to the incomplete characterization of the residues encountered in plant tissues; significant percentages of extractable radioactivity (usually very polar in nature) could not be identified and no attempts were made to determine the nature of unextractable radioactivity. The following additional data are required:

- Data involving the reasonably complete characterization of the extractable and unextractable radioactive residues found in plant tissues as the result of the application of radiolabeled pendimethalin in a manner simulating a treatment regime registered for use. Representative crops (potatoes, soybeans, corn, etc.) for which pendimethalin formations are registered should be used.

The available plant metabolism data do show that pendimethalin residues are absorbed and translocated by plants based on studies of corn, cotton, dry beans, lima beans, peanuts, potatoes, red table beets, rice, snapbeans, soybeans, sugarcane, and wheat.

The molecular structures of pendimethalin and its known metabolites are depicted in Table 1 (attached to this section). Identified metabolites occurring in plants, based on the data submitted, include 4-[(1-ethylpropyl) amino]-2-methyl-3,5-dinitrobenzyl alcohol (CL 202,347), 3-[(1-ethylpropyl) amino]-6-methyl-2,4-dinitrobenzyl alcohol (CL 217,146), 4-[(1-ethylpropyl) amino]-3,5-dinitro-o-toluic acid (CL 99,900), 4-[(1-ethyl-2-hydroxypropyl) amino]-3,5-dinitro-o-toluic acid (CL 113,072), 3-(2,6-dinitro-3,4-xylidino)-2-pentanol (CL 113,066), 4-[(1-ethyl-2-hydroxypropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol (CL 113,067), and 4-[(1-ethyl-3-hydroxypropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol (CL 113,068).

Table 1. Pendimethalin and its metabolites.

Identification number	Structure	Chemical Name	Abbreviation
CL 92,553		N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine	pendimethalin
CL 202,347		4[(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol	3,5-dinitrobenzyl alcohol
CL 217,146		3[(1-ethylpropyl)amino]-6-methyl-2,4-dinitrobenzyl alcohol	2,4-dinitrobenzyl alcohol
CL 99,900		4[(1-ethylpropyl)amino]-3,5-dinitro-o-toluic acid	4-carboxylic acid
CL 113,072		4[(1-ethyl-2-hydroxypropyl)amino]-3,5-dinitro-o-toluic acid	--
CL 113,066		3-(2,6-dinitro-3,4-xylidino)-2-pentanol	--
CL 113,067		4-[(1-ethyl-2-hydroxyprooyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol	--
CL 113,068		4-[(1-ethyl-3-hydroxyprooyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol	--
CL 113,071		4-[[(1-carboxymethyl)propyl]amino]-3,5-dinitro-o-toluic acid	--
CL 202,078		4-amino-3,5-dinitro-o-toluic acid	--
CL 202,345		4-[(1-ethyl-3-hydroxyprooyl)amino]-3,5-dinitro-o-toluic acid	--

All plant tolerances, excluding peanut hulls, tentatively should continue to be expressed in terms of the combined residues of the parent compound (CL 92,553) and its 3,5-dinitrobenzyl alcohol metabolite (CL 202,347). The tolerance for peanut hulls is expressed in terms of the parent (CL 92,553), the 3,5-dinitrobenzyl alcohol metabolite (CL 202,347), and the 2,4-dinitrobenzyl alcohol metabolite (CL 217,146). The EPA Toxicology Branch considers the CL 217,146 metabolite as well as the CL 113,072 metabolite (also a significant component in peanut hulls) not to be "of undue toxicological concern" (memorandum from J. Doherty [Toxicology Branch/HED] to R. Taylor [Registration Division] in response to a RCB deferral of February 20, 1981; correspondence file of PP# 6F1741); based on this memorandum, CL 217,146 should be deleted from the peanut hull tolerance. Note that a final determination of the residues of concern in or on plants cannot be made until receipt of the requested plant metabolism data.

References (used):

Adams, C.F. and S.K. Eisner. 1975. PROWL® herbicide, potato metabolism: residual radioactivity in potato plants grown in soil treated with carbon-14 labeled PROWL. Report No. C-728. Unpublished study submitted by American Cyanamid Co. under PP#6G1739. (CDL No. 095485-X; MRID No. 00039537).

Adams, C.F. and S.K. Eisner. 1975. PROWL® herbicide lima bean metabolism: residual activity in lima bean pods and plants grown in soil treated with carbon-14 labeled PROWL. Report No. C-729. Unpublished study submitted by American Cyanamid Co. under PP#6G1739. (CDL No. 095485-U; MRID No. 00039535).

Barringer, Jr., D.F. and S. Eisner. 1973. CL 92,553: Metabolism IV. Uptake and residues of radioactivity in sweet corn grown in soil treated with carbon-14 labeled PROWL herbicide. Unpublished study submitted by American Cyanamid Co. under PP#5F1556. (CDL Nos. 070070-D and 094470-A; MRID Nos. 00106779 and 00074621).

Barringer, Jr., D.F. and S.K. Eisner. 1974. CL 92,553: Metabolism IX. Uptake and residues of radioactivity in red table beets grown in soil with aged residues of carbon-14 labeled CL 92,553 (PROWL* herbicide). A rotational crop study. Exhibit No. 25. Unpublished study submitted by American Cyanamid Co. under PP#5F1556. (CDL No. 094470-A; MRID No. 00106779).

Barringer, Jr., D.F. and S.K. Eisner. 1975. CL 92,553: Metabolism XIV. Uptake and residues of radioactivity in winter wheat grown in soil treated with carbon-14 labeled PROWL® herbicide. Unpublished study submitted by American Cyanamid Co. under EPA Reg. No. 241-EX-95. (CDL No. 098994-B; MRID No. 00108317).

Gatterdam, P.E., Fasinski, R. and R.E. Tondreau. 1973. CL 92,553: Metabolism II. Uptake and residues of radioactivity in cotton following incorporation of carbon-14 CL 92,553 in soil. Unpublished study submitted by American Cyanamid Co. under PP#5F1556. (CDL No. 094475-E; MRID No. 00046278).

Kapoor, I.P. and S.K. Eisner. 1974. CL 92,533: Metabolism VIII. Uptake and residues of radioactivity in cotton grown in soil treated with carbon-14 labeled PROWL* herbicide. Unpublished study submitted by American Cyanamid Co. under PP#5F1556. (CDL Nos. 094475-G and 094470-A; MRID Nos. 00106779 and 00046280).

Mangels, G. 1981. PROWL* pendimethalin (CL 92,553): residual radioactivity in dry beans treated preplant incorporated with carbon-14 CL 92,553 PROWL herbicide. American Cyanamid Co. Report No. PD-M Vol. 18-7 submitted under PP#1F2567. (No MRID assigned).

Mangels, G. 1982. PROWL* pendimethalin (CL 92,553): residual radioactivity in sugarcane treated preemergence incorporated and at layby with carbon-14 CL 92,553 PROWL herbicide. American Cyanamid Co. Report No. PD-M Vol. 19-11 submitted under PP#3F2765. (No MRID assigned).

Mangels, G. and L. Lucas. 1980. PROWL® pendimethalin (CL 92,553): residual radioactivity in rice grain and plants treated postemergence with carbon-14 CL 92,553 PROWL. Unpublished study submitted by American Cyanamid Co. under EPA Reg. No. 241-243. (CDL No. 099888-D; MRID No. 00071121).

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Discussion of the data:

In a study conducted by Mangels and Lucas (1980, MRID No. 00071121), rice was grown from seed in tanks under greenhouse conditions and treated with a foliar application of [^{14}C]pendimethalin (labeled in the 3,4-dimethyl groups) at 1 lb ai/A when plants were at the three- to four-leaf stage (1 month following

planting). Two weeks after treatment, the plants were placed outdoors and flooded with water 2-3 inches deep. They were returned to the greenhouse, because of cool weather, 5 months after planting. After appropriate intervals, total ^{14}C was determined in plant and grain samples. Plant samples collected 2 and 4 weeks after treatment were extracted three times with methanol using a homogenizer and twice with HCl in methanol before being radioassayed. Samples of water collected 14 weeks (heading stage) after treatment contained nondetectable ^{14}C (<0.001 ppm). Plant samples collected 2 and 4 weeks following treatment contained 20.97 and 2.077 ppm of radioactivity (pendimethalin equivalents), respectively, and a plant sample collected after 14 weeks contained 0.016 ppm. Extractable radioactive residues in the plant samples decreased from 85.2% at 2 weeks to 47.7% at 4 weeks. Straw collected 23 weeks after treatment contained 0.025 ppm of radioactive residues. Samples of rice heads collected after 14 weeks contained <0.01 ppm of radioactivity and samples of rice grain and hulls collected after 23 weeks contained 0.022 and 0.028 ppm of radioactive residues, respectively. Characterization of residues in hulls, grain, and straw was not performed because levels were too low for chromatographic analysis.

Zulalian and Eisner (1973, MRID No. 00106779) investigated the uptake and distribution of radioactivity in cotton and soybeans greenhouse-grown from seed in soil treated with [^{14}C]pendimethalin (labeled in the 4-methyl position) at 1 lb ai/A (broadcast application) ~4 months prior to planting; aged radioactive residues were used in order to determine if pendimethalin residues are taken up from soil into rotational crops. Plant samples were extracted three times with ethyl alcohol using a homogenizer. Cottonseed and soybeans were extracted three times using chloroform-methanol and the extracts were partitioned between acetonitrile and hexane. Ethyl alcohol extracts were analyzed for radioactivity by liquid scintillation counting (LSC); other solvent extracts and unextractable material were combusted prior to LSC analysis. Total radioactive residues (pendimethalin equivalents) in cotton plant samples (leaves, petioles, and stalks) collected 16-32 days after planting were at 0.116-0.145 ppm (includes 0.077-0.087 ppm as ethyl alcohol-extractable and 0.029-0.068 ppm as nonextractable) and in a sample collected after 62 days were 0.061 ppm (includes 0.042 ppm as ethyl

alcohol-extractable and 0.019 ppm as nonextractable). In cottonseed collected 132 days after planting, total radioactive residues were at 0.016 ppm. Of the total radioactivity recovered from cottonseed, 80% partitioned into acetonitrile and 20% into hexane. Total radioactive residues in or on soybean plants (leaves and stems) were at 0.152-0.337 ppm (includes 0.081-0.291 ppm as ethyl alcohol-extractable and 0.046-0.071 ppm as nonextractable) 16-32 days after planting and were at 0.087 ppm (includes 0.051 ppm as ethyl alcohol-extractable and 0.036 as nonextractable) 62 days after planting. Soybeans contained 0.06 ppm of radioactive residues (includes 0.025 ppm as extractable and 0.035 ppm as nonextractable) 132 days following planting. Of the total radioactivity recovered from soybeans, 20% was partitioned into acetonitrile and 80% into hexane; this distribution was opposite of that observed in cottonseed.

Marei and Eisner (1974, Report No. C-538 in MRID No. 00029803) conducted a greenhouse study involving levels of radioactivity in soybean pods and foliage from plants grown in soil treated with 12.25 mg of [^{14}C]pendimethalin (EC; labeled in the 4-methyl position); this rate was stated as being equivalent to 1.5 lb ai/A as a preplant-incorporated treatment. Samples of whole plants and whole pods were extracted with methanol and analyzed by combustion and LSC. Whole plant samples were further analyzed by TLC in order to determine the identity of the radioactive residues present. Whole plant samples contained 0.10 ppm pendimethalin equivalents (includes 0.05 ppm of methanol-extractable radioactivity and 0.05 ppm of unextractable radioactivity) 4 weeks after treatment and 0.12 ppm (includes 0.06 ppm of methanol-extractable radioactivity and 0.06 ppm of unextractable radioactivity) 8 weeks after treatment. Samples of soybean pods collected after 8 weeks contained 0.04 ppm (includes 0.02 ppm of methanol-extractable radioactivity and 0.02 ppm of unextractable radioactivity). Control values for whole plant samples were at 0.03 and 0.02 ppm after 4 and 8 weeks, respectively, and for pod samples were at 0.02 ppm. Data involving the characterization of radioactive residues were not presented but it was stated that the plant extract contained trace amounts of pendimethalin.

Mangels (1982, PP#3F2765) performed an investigation of radioactive residues in or on sugarcane as a result of a preemergence incorporated application of [^{14}C]pendimethalin (labeled in the 3,4-dimethyl groups) at 3 lb ai/A only or followed by a layby application 3 months later at the same rate. Samples of sugarcane from the two plots treated were collected at maturity (6 and 9 months after treatments) and rinsed with water to remove any soil present, ground in a blender, combusted, and analyzed by LSC. Levels of radioactivity (pendimethalin equivalents) in the samples collected were at <0.01 ppm as the result of both treatment regimes. Identification of any residues present was not possible.

Adams and Eisner (1975, Report No. C-729 in MRID No. 00039535) conducted a greenhouse study involving levels of radioactivity in lima bean pods and foliage grown from seed in pots of soil treated with 14.3 mg of [^{14}C]pendimethalin (EC; labeled at the 4-methyl); this dose was stated as being equivalent to 1.5 lb ai/A as a preplant incorporated treatment. Samples were extracted with methanol and then with HCl in methanol using a homogenizer. The extracts and remaining residues were analyzed by combustion and LSC. Total pendimethalin equivalents (includes extractable and unextractable material) were at 0.15 ppm after 30 days and 0.39 ppm after 60 days in samples of foliage; levels in untreated control plants were at 0.14 ppm after 30 days and at 0.07 ppm after 60 days. Of the total 0.39 ppm of radioactivity found in foliage samples collected after 60 days, 0.20 ppm was methanol-extractable, 0.11 ppm was HCl-methanol-extractable, and 0.08 ppm was unextractable. Lima bean pods collected 60 days after treatment contained 0.08 ppm of radioactivity of which 0.02 ppm was methanol-extractable, 0.01 ppm was HCl-methanol-extractable, and 0.05 ppm was unextractable; pods from control plants contained 0.04 ppm of radioactivity. No attempt was made to identify the radioactive residues present.

Adams and Eisner (1975, Report No. C-728 in MRID No. 00039537) performed an investigation of levels of radioactivity in potato plants grown (from seed pieces) in a greenhouse in soil treated with 41.5 mg of [^{14}C]pendimethalin (EC; labeled at the 4-methyl) in acetone solution; the dose was equivalent to 2 lb ai/A as a preemergence treatment. The method of extraction and ana-

lysis was identical to that used for lima bean plants described previously. The total radioactivity found in foliage was at 0.58 ppm (includes 0.46 ppm as methanol-extractable, 0.06 ppm as HCl-methanol-extractable, and 0.06 ppm as unextractable) in samples collected 30 days following treatment and at 0.37 ppm (includes 0.18 ppm as methanol-extractable, 0.07 ppm as HCl-methanol-extractable, and 0.12 ppm as unextractable) in samples collected after 60 days. Control samples contained 0.22 ppm and 0.05 ppm of radioactivity after 30 and 60 days, respectively. No attempt was made to identify the radioactive residues present.

Zulalian et al. (1978, MRID No. 00106795) conducted a study involving potatoes grown in soil treated with [^{14}C] and/or [^{13}C]pendimethalin under both greenhouse and field conditions. In the greenhouse experiment, seed pieces were placed in soil treated with 41 mg of [^{14}C]pendimethalin (EC; labeled in the 4-methyl position) in acetone solution which was equivalent to 2 lb ai/A as a preemergence treatment. In the field experiment, seed pieces were planted in soil treated with a mixture of [^{14}C] and [^{13}C]pendimethalin (formulated as a 4 lb/gal EC; labeled in the 4-methyl and 3-methyl, respectively) at 1 lb ai/A. Samples grown under greenhouse conditions were extracted twice with methanol and once with HCl in methanol using a homogenizer. Samples grown under field conditions were extracted three times with HCl-methanol in a homogenizer. The unextractable residue remaining was combusted. Radioactivity in all samples was determined by LSC. TLC was used to identify residues (using a solvent system of benzene:dioxane:acetic acid [90:30:1]). Potato tubers grown under greenhouse conditions and harvested at maturity (120 days) contained pendimethalin equivalents at 0.13 ppm (includes 0.08 ppm as methanol-extractable, 0.01 ppm as HCl-methanol-extractable, and 0.04 ppm as unextractable); control samples contained 0.04 ppm of radioactivity. Potato tubers grown in-field contained 0.10 ppm (includes 0.08 ppm as HCl-methanol-extractable and 0.02 ppm as unextractable) of radioactivity 93 days following treatment and 0.08 ppm (includes 0.06 ppm as HCl-methanol-extractable and 0.02 ppm as unextractable) after 106 days; control values were at 0.01-0.02 ppm. TLC analysis of the methanol extract from potato tubers grown in the greenhouse revealed the presence of pendimethalin only. Radioactivity in field-grown potatoes was too low for TLC analysis.

Mangels (1981, PP#1F2567) studied the residual radioactivity in dry beans greenhouse-grown from seed in soil treated (preplant incorporated) with [^{14}C]pendimethalin (labeled in the 3,4-dimethyl groups) at 1.5 lb ai/A. Samples of dry beans were collected at harvest, separated from the pod, ground, and radioassayed using combustion and LSC. Total radioactive residues in or on the dry beans were at 0.03 ppm. This level was too low to permit chromatographic characterization of residues.

While the above studies do not characterize the radioactive residues present, they do clearly demonstrate that pendimethalin residues are absorbed from both soil and foliar treatments and are translocated throughout plants. All residue values were expressed in terms of pendimethalin equivalents. The following studies not only provide further evidence of absorption and translocation, they attempt to determine the nature of the residues present as a result of radiolabeled treatments with pendimethalin.

Mangels and Lucas (1981, MRID No. 00093698) performed a field study involving radioactive residues in or on sweet corn plants, cobs, and grain following a postemergence foliar application using [^{14}C]pendimethalin (4 lb/gal EC formulation; labeled in the 3,4-dimethyl groups) at 1.5 lb ai/A. The soil around the plants was raked after treatment to incorporate [^{14}C]pendimethalin. Samples were collected 2, 6, and 12 weeks following treatment, frozen, macerated, and analyzed for radioactivity by LSC. The sample collected at the 2-week interval was extracted three times with methanol and twice with HCl in methanol and extract aliquots were radioassayed. Extracts were combined and partitioned between water and methylene chloride and then the methylene chloride fraction was analyzed by two dimensional TLC (solvent systems were methylene chloride:methanol [75:25] vs. toluene:p-dioxane:acetic acid [90:30:1] and ethyl acetate:n-propanol:water:formic acid [30:50:15:5] vs. ethyl acetate:n-propanol:water:ammonium hydroxide [30:50:15:5]). Levels of radioactivity (pendimethalin equivalents) in or on corn plants decreased from 3.15 ppm at 2 weeks to 0.04 ppm at 12 weeks (harvest of fodder). A silage sample collected 6 weeks posttreatment contained 0.02 ppm of radioactivity. In samples of cobs and grain collected after 12 weeks, levels of radioactivity were <0.01 ppm (presumably, this is nondetectable). The radioactivity (3.15

ppm) in the corn plant sample collected at the 2-week interval was found to consist of 67% extractable residues and 33% nonextractable residues. TLC analysis of the extractable material revealed 6% (0.12 ppm) as pendimethalin, 3% (0.06 ppm) as the 3,5-dinitrobenzyl alcohol metabolite (CL 202,347), and 2% (0.04 ppm) as the 2,4-dinitrobenzyl alcohol metabolite (CL 217,146). The radioactive residue remaining was described as consisting of unidentified highly polar material; conjugates were not sought. Analysis was not performed to identify radioactive residues in samples collected at other time intervals because of the low radioactivity levels encountered.

Barringer, Jr. and Eisner (1973, MRID Nos. 00106779 and 00074621) performed a study involving radioactivity in or on sweet corn grown from seed under greenhouse conditions in soil treated with [^{14}C]pendimethalin labeled in the 4-methyl or N-propyl position at ~1.5 lb ai/A or ~1.6 lb ai/A, respectively. Plant samples were collected, extracted with acetone:methanol (1:1) using a homogenizer, re-extracted twice with acetone:methanol, and extracted once with HCl in methanol (mature corn samples were not subjected to the acid extraction). Extracts (initial) were partitioned between water and chloroform and the chloroform fractions were partitioned between acetonitrile and n-hexane. The hexane fractions were extracted twice with acetonitrile. This procedure was done in order to separate the radioactivity (contained in the acetonitrile) from the plant oils, waxes, and some chlorophyll (contained in the hexane). In order to remove co-extracted plant tissues, the acetonitrile fractions were subjected to further cleanup by precipitation, chloroform extraction, and treatment with activated charcoal in benzene; this separated the radioactivity in the acetonitrile fraction into either chloroform or benzene. TLC analysis employed the following solvent systems: (i) xylene:-chloroform:methanol (80:20:2) vs. 1,2-dichloroethylene (cis, trans mixture):-carbon tetrachloride:nitromethane (30:10:10), low polarity, and (ii) chloroform:methanol:water (75:22:3) vs. chloroform:acetone:acetic acid (60:30:10), high polarity. Radioactive residues (total) were <0.02-0.05 ppm (includes 0.02-0.04 ppm as extractable and ≤0.01 ppm as unextractable in or on whole corn plant samples collected 1-2 months after planting (4-methyl labeled treatment). Radioactive residues (total) were 0.03 ppm (includes 0.01 ppm as extractable and 0.02 ppm as unextractable) in or on green plant parts,

<0.02 ppm (includes <0.01 ppm as extractable and 0.01 ppm as unextractable) in or on grain, and <0.02 ppm (includes <0.01 ppm as extractable and <0.01 ppm as unextractable) in or on cobs from samples harvested 81 days after planting; the data represents both radiotracer treatments. From plant samples collected 1-2 months after planting (4-methyl radiotracer treatment), 76-81% of the radioactivity present was extractable (methanol/acetone and methanol/HCl extractions combined) and 19-24% was unextractable; 64-66% of the extracted radioactivity partitioned into chloroform and 34-36% into water. In a plant sample harvested after 81 days, 45% of the radioactivity was extractable (methanol/acetone) and 55% was unextractable; the decrease in extractable residues observed in this sample may have been due to the absence of the methanol/HCl extraction used for the 1- and 2-month samples. TLC analysis of the chloroform-partitioned radioactivity from the 1-month sample, revealed the presence of pendimethalin and its CL 202,347 metabolite representing 49-74% and 5-7%, respectively, of the radioactivity present along with a more polar unidentified compound constituting 4-5%. The water-soluble portion of the extract from this sample was subjected to methanol extraction, acidification, and methylation using diazomethane which resulted in 74% of the radioactivity from the water fraction partitioning into chloroform; the authors stated that this suggested that the majority of radioactivity in the water-soluble fraction consisted of carboxylic acids or phenols (TLC analysis of the methylated products resulted in four or more spots, none of which were identified). The water-soluble fraction from the 2-month plant sample was subjected to acid hydrolysis which converted 10.2% of the radioactivity to chloroform-soluble radioactivity. Enzyme hydrolysis (β-glucosidase and hemicellulase) converted 8.2% of the ^{14}C to chloroform-soluble and reaction with diazomethane converted 40.8%; the authors concluded that these results suggested that the water-soluble radioactivity consisted of a significant amount of acidic material and that little, if any, were conjugates. We require that further attempts be made to identify polar and unextractable residues (unidentified radioactivity accounted for ~65% of the total ^{14}C).

Barringer, Jr. and Eisner (1974, MRID No. 00106779) conducted a similar study involving the uptake and distribution of aged radioactive residues by red table beets greenhouse-grown from seed in soil treated 181 days (~6

months) earlier with [^{14}C]pendimethalin (labeled in the 4-methyl position) at 1.5 lb ai/A (broadcast) just after the planting of sweet corn. The corn was harvested 100 days prior to the red table beet planting; this study was intended to simulate the pendimethalin residues found in red table beets grown as a rotational crop. The levels of radioactive residues (pendimethalin equivalents) found in the sweet corn are discussed in the previously described study by Barringer, Jr. and Eisner (1973, MRID Nos. 00106779 and 00074621). Plant samples were extracted with methanol:acetone (1:1) using a blender, and the beet root sample collected 5 months postplant was extracted with methanol. Radioactivity was determined by combusion and LSC; characterization of the radioactive residues was performed by TLC using toluene:chloroform:methanol (80:20:2) vs. 1,2-dichloroethylene (cis, trans mixture):carbon tetrachloride:-nitromethane (30:10:10) or using benzene:dioxane:acetic acid (90:30:1). Beet foliage contained radioactive residues of 0.21 ppm (includes 0.14 ppm as extractable and 0.07 ppm as nonextractable) 30 days after planting and 0.03 ppm after 90 days. Red beet root samples contained radioactive residue levels of 0.06 ppm after 90 days and 0.04 ppm after 5 months. TLC analysis revealed that 52% of the radioactive residues in the 30-day beet foliage sample consisted of pendimethalin and 6% was the 3,5-dinitrobenzyl alcohol metabolite; 12% consisted of three unidentified compounds and 30% was material that remained at the origin. A total of ~61% of the ^{14}C was unidentified.

Gatterdam et al. (1973, MRID No. 00046278) investigated the uptake of radioactivity by cotton plants grown in soil (under greenhouse conditions) treated with either [^{14}C]pendimethalin labeled in the 4-methyl position (2.03 mg dose) or [^{14}C]pendimethalin labeled in the N-propyl position (2.08 mg dose); dosages were equivalent to 1 lb ai/A as a broadcast application. After appropriate sampling intervals, plant and boll samples were homogenized with methanol, extracted twice with methanol, and extracted twice with HCl in methanol. The methanol extracts were partitioned between water and chloroform. Radioactivity was determined by combusion and LSC. Cottonseed removed from bolls were extracted three times with chloroform-methanol. GC analysis (using an electron capture detector) was performed to determine the nature of the radioactivity present in the chloroform extract from plants

sampled after two weeks (radioactivity in organosoluble fractions from other plant samples was too low for reliable analysis). Samples of bolls (bracts and caps) contained 2.61-2.91 ppm, seeds contained 0.24-0.32 ppm, and lint contained 0.17-0.23 ppm of radioactivity (pendimethalin equivalents) 16-17 weeks following treatment; this combined data represents cotton plants treated with 4-methyl and N-propyl labeled [^{14}C]pendimethalin. Plants (whole) harvested 2-8 weeks after treatment with 4-methyl labeled [^{14}C]pendimethalin contained total ^{14}C at 0.197-0.231 ppm (includes 0.122-0.18 ppm as extractable and 0.017-0.116 ppm as unextractable). These values were much higher than the 0.05 ppm contained in the single plant sample collected following treatment with N-propyl labeled [^{14}C]pendimethalin and a sampling interval of 4 weeks. Levels of radioactivity in total plant (without bolls) samples collected after 16-17 weeks were at 0.116 ppm and 0.262 ppm following treatment with 4-methyl labeled [^{14}C]pendimethalin and N-propyl labeled [^{14}C]pendimethalin, respectively. Extractable radioactivity (methanol and HCl-methanol) decreased in plant samples (4-methyl [^{14}C]pendimethalin treatment) from 91.4% at 2 weeks posttreatment to 70.7% at 17 weeks. In addition, a larger portion of the extracted radioactivity from mature plants (61-69%) partitioned into water from chloroform than did that from immature plants (12-48%); this data represents both radiotracer treatments which suggested the presence of more polar metabolites in the mature plants. In or on cotton bolls (bracts and caps) collected 16-17 weeks after treatment, 99.7% of the recovered radioactivity was extractable and 0.3% was unextractable as the result of treatment with 4-methyl labeled [^{14}C]pendimethalin, and 1.2% was extractable and 98.8% was unextractable as the result of treatment with N-propyl labeled [^{14}C]pendimethalin. The difference in radioactive extractability between the two different radiotracers used indicates that the N-ethylpropyl side chain had been cleaned. This further indicates that the parent compound or any closely related metabolites were present in small quantities. GC analysis of the chloroform extract (only 47% of the total recovered radioactivity was present after cleanup) from the 2-week plant sample indicated that 25% (0.021 ppm) of the extracted radioactivity was pendimethalin (background interferences were encountered).

In a study conducted by Kapoor and Eisner (1974, MRID No. 00106779), cotton plants were grown in a greenhouse in soil treated with [^{14}C]pendimethalin (labeled in the 4-methyl position) at 1 lb ai/A. After sampling intervals of 2, 4, 8, and 19 (maturity) weeks, plants were extracted twice with methanol and once with HCl in methanol using a homogenizer before being analyzed by LSC for radioactivity. Cotton bolls were collected at the 19-week interval and separated into seeds, lint, boll cap, and bract before being combusted and analyzed by LSC or being extracted with methanol and assayed for radioactivity. TLC was employed to characterize the residues in the plant extracts using benzene:dioxane:acetic acid (90:30:1). The major metabolite from the cotton bract sample was analyzed further by GC/MS. Cotton plants contained 0.09 ppm of total radioactivity (pendimethalin equivalents) at 2 weeks, 0.06 ppm at 4 weeks, 0.04 ppm at 8 weeks, and 0.07 ppm at 19 weeks (harvest). Of the total radioactivity present in or on the 2-week sample, 97% was extractable (89% in methanol and 8% in methanol/HCl) and 3% was unextractable; these proportions of extractable residues had decreased by 19 weeks to 69% (49% in methanol and 20% in methanol/HCl) while unextractable residues increased to 31%. Analysis using TLC revealed the presence of pendimethalin (0.02 ppm at 2 weeks and 0.01 ppm at both 4 and 8 weeks) and its 2,4-dinitrobenzyl alcohol metabolite (0.01 ppm at 2 weeks and <0.01 ppm at both 4 and 8 weeks) in the methanol extracts from cotton plants. Unidentified nonmigrating compounds were observed in the 2-week sample at 0.04 ppm, in the 4-week sample at 0.03 ppm, and in the 8-week sample at 0.02 ppm; an unidentified migrating compound was also observed in the 2-week sample at 0.02 ppm. Further characterization of the polar metabolites found was not possible due to the low levels present; 67% of the total ^{14}C was unidentified. Cotton bolls collected after 19 weeks contained 9.64 ppm of radioactivity in the bract, 0.06 ppm in the cap, 0.08 ppm in the seed, and 1.75 ppm (1.67 ppm was methanol-extractable) in the lint. TLC analyses of the methanol washing from cotton lint indicated that the radioactivity present was due to the parent, pendimethalin. The methanol extract from the bract, which was subjected to TLC analysis, also contained the parent compound; this was confirmed by GC/MS analysis.

Marei et al. (1974, MRID No. 00067293) performed a study of radioactivity found in rice plants and grain grown from seedlings in soil (contained in tanks) treated with [^{14}C]pendimethalin under greenhouse conditions. A granu-

lar application equivalent to 3 lb ai/A was made to one tank using [^{14}C]pendimethalin labeled in the 4-methyl position and to two tanks using [^{14}C]pendimethalin labeled in the N-propyl position. The tanks were maintained at a flooded depth of 2 inches for a 4-month period and then allowed to evaporate. Plant samples were collected 4, 8, and 20 weeks after treatment and extracted three times with methanol using a homogenizer. Rice seeds and hulls were collected from the 20-week plants at the time of harvest. The radioassay procedure used involved combusion and LSC. Analysis by TLC (employed methylene chloride:methanol [3:1] vs. benzene:dioxane:acetic acid [90:30:1]) was used to characterize the radioactivity present. Levels of total radioactivity (pendimethalin equivalents) increased from 0.17 ppm (0.10 ppm was extractable) at 4 weeks to 0.36 ppm (0.14 ppm was extractable) at 20 weeks in plants receiving the 4-methyl labeled treatment and from 0.21 ppm (0.13 ppm was extractable) at 4 weeks to 0.39 ppm (0.15 ppm was extractable) at 20 weeks in plants receiving the N-propyl labeled treatment; the higher concentrations in the 20-week mature plant samples may have been due only to the dryness of these samples because calculations are based on plant wet weight and the younger plants (4- and 8-week samples) had higher moisture contents. Whole rice seeds from plants collected after 20 weeks contained 0.05 ppm of radioactivity; the seeds and hulls, when analyzed separately, contained 0.04 and 0.02-0.03 ppm, respectively. Results were nearly identical for each radiotracer treatment and, therefore, were combined. TLC analysis of the plant extract samples revealed that pendimethalin and its 4-carboxylic acid metabolite (CL 99,900) each represented 30% of the radioactivity present while the remaining 40% was unidentified material which did not migrate from the origin. The unidentified material was combined with diazomethane but this did not cause the material to migrate from the origin. About 70% of the total plant ^{14}C was unidentified (either unextractable or nonmigrating polar material). Water samples were collected from each tank after 8 weeks, extracted with methanol, and the extract was analyzed by TLC. Soil samples were taken after 7 months, extracted three times with methanol and three times with HCl in methanol, and the extracts were analyzed by TLC (using methylene chloride:petroleum ether [2:1] vs. benzene:dioxane:acetic acid [90:30:1]). Radioactivity in soil and water samples was determined directly by LSC. Water samples contained ~0.10 ppm of radioactivity for both radiotracer treatments after 1

month and ~0.01 ppm 3 months following application. TLC analysis of water samples revealed the presence of four compounds, only two of which were identified (pendimethalin and the 4-carboxylic acid metabolite CL 99,900); exact amounts of radioactivity present were not provided. In soil samples collected 7 months after treatment, six unknown compounds and material that remained at the origin were found along with pendimethalin and its 4-carboxylic acid metabolite which represented 47.6-60.7% and 3.2-6.9% of the radioactivity extracted by methanol (from both radiotracer treatments), respectively.

Zulalian (1980, PP# 1F2567) conducted a metabolism study of snap bean plants field-grown in soil treated with a preplant incorporated application of a mixture of [^{13}C] and [^{14}C]pendimethalin (labeled in the 3- and 4-methyl groups, respectively) at 1 lb ai/A. Use of [^{13}C]pendimethalin was for metabolite identification by MS as a "mass marker". Subsamples of bean foliage and pods were extracted with HCl in methanol using a homogenizer, filtered, and the remaining plant material extracted twice again. Radioassay was performed by combustion/LSC or direct counting using LSC. Extracts (HCl/methanol) from plants collected 64 days after planting (106 days after treatment) were subjected to a hydrolysis experiment by heating and refuxing for 4 hours, then cooling and adding sodium hydroxide and adjusted to pH 5. TLC analysis was performed using a solvent system of chloroform:acetone:acetic acid (180:90:-30). Plant samples 29 days old (71 days after treatment) contained 0.10 ppm of total radioactive residues (includes 0.08 ppm as acid methanol-extractable and 0.02 ppm as unextractable) and plant samples 64 days old (106 days after treatment) contained 0.20 ppm (includes 0.16 ppm as acid methanol-extractable and 0.04 ppm as unextractable). Total radioactive residues in or on mature bean pods (collected 64 days after planting) were at 0.03 ppm (includes 0.02 ppm as acid methanol-extractable and 0.01 ppm as unextractable). Because residue levels in 29-day old plant samples and mature bean pods were too low, characterization of residues by TLC was performed for the 64-day old samples which resulted in only one radioactive band that did not correspond to any of 54 related compounds or to pendimethalin itself. Analysis by GC of the unhydrolyzed and hydrolyzed extracts from the 64-day old plants for pendimethalin and its CL 202,347 metabolite resulted in nondetectable (<0.05 ppm) values of radioactive residues that partitioned with chloroform from the water phase. Therefore, none of the ^{14}C residues were characterized.

Barringer and Eisner (1975, MRID No. 00108317) conducted a study involving levels of radioactivity in winter wheat greenhouse-grown from seed in soil treated with either [^{14}C]pendimethalin labeled in the 4-methyl position at 1.48 lb ai/A or [^{14}C]pendimethalin labeled in the N-propyl position at 1.38 lb ai/A. Twelve days after planting, the seedlings were placed outdoors for winter chilling and after 2 months were returned to the greenhouse. Samples were extracted with methanol and the extracts were partitioned between water and ethyl acetate. Radioactivity was determined using combustion and LSC. Identification of residues was performed by TLC (using methylene chloride:-petroleum ether [2:1] vs. benzene:dioxane:acetic acid [90:30:1]). Plant top samples contained 0.14-0.19 ppm (includes 0.12-0.14 ppm as methanol-extractable and 0.02-0.05 ppm as unextractable) of radioactivity (pendimethalin equivalents) 30 days after breaking winter dormancy and 0.05-0.18 ppm (includes 0.02-0.16 as methanol-extractable and 0.02-0.03 ppm as unextractable) after 60 days. Mature wheat grain and hulls (collected 120 days after breaking winter dormancy) contained 0.01-0.02 ppm and 0.05-0.09 ppm, respectively, of radioactivity. Samples of straw also harvested at the 120-day interval contained 0.07-0.15 ppm (includes 0.05-0.06 ppm as methanol-extractble and 0.01-0.10 ppm as unextractable) of radioactivity. In wheat plant samples harvested 1 month after breaking winter dormancy, 51-52% of the extracted radioactivity partitioned into ethyl acetate and 48-49% into water. The extracted radioactivity from the samples was found to consist of (determined by TLC) 11-13% pendimethalin and 87-89% polar metabolites (remained at the origin). Further analysis was performed to determine the nature of the large fraction of polar metabolites present. The ethyl acetate and water fractions partitioned from the extracts were found to contain compounds that possessed neither acidic or basic characteristics after analysis using high-voltage paper electrophoresis at pH 2.1, 8.0, and 11.9. Of the water-soluble radioactivity, 15% and 56% was converted to organosoluble products (methylene chloride-soluble) upon hydrolysis using β-glucosidase plus hemicellulase and 1 N HCl, respectively. The hydrolysis products were found not to react with diazomethane but did react with acetic anhydride which suggested that the polar metabolites were conjugates of alcoholic compounds and that alcohols (and possibly amino acids) had been released by hydrolysis. TLC analysis indicated the presence of nine compounds in the hydrolysate, one of which was

identified as pendimethalin's benzyl alcohol metabolite (CL 202,347) and six that displayed mobility similar to the acetates of alcohols (used as standards). Therefore, ~89% of the ^{14}C was unidentified material.

Marei et al. (1975, MRID Nos. 00051965, 00051963, 00031219, and 00109915) investigated levels of radioactivity in peanut seeds and foliage grown under greenhouse conditions in soil treated with 18 mg of [^{14}C]pendimethalin labeled in the 4-methyl position; this dosage is equivalent to 0.75 lb ai/A. Plants were sampled after 4 and 8 weeks and pods were sampled after ~14 weeks (at maturity). Samples were extracted three times with methanol using a homogenizer and were analyzed for radioactivity by combustion and LSC. TLC was employed for identification of the radioactive residues present; the solvent system used was methylene chloride:methanol (3:1) vs. benzene:dioxane:-acetic acid (90:30:1). Levels of radioactivity (pendimethalin equivalents) were 0.13 and 0.10 ppm in or on immature peanut plants collected after 4 and 8 weeks, respectively. In or on mature plants collected 14 weeks after treatment, radioactive levels were at 0.21 ppm. The major portions of radioactive residues in all plant samples were methanol-extractable ranging from 0.06 to 0.08 ppm for immature plant samples and at 0.11 ppm for mature plants. Peanut hulls collected at the 14-week harvest contained 1.65 ppm of radioactivity (0.88 ppm as unextractable) and peanut seeds contained 0.16 ppm (0.10 ppm as unextractable). Identification by TLC of residues in the extract from 14-week plant samples resulted in pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite (CL 202,347) representing 30 and 11%, respectively, of the radioactivity present along with 59% unidentified material. Analysis of the extract from peanut hulls revealed the presence of seven metabolites representing a total of 0.77 ppm, which included 12.2% as pendimethalin, 7.3% as CL 202,347, 0.9% as the 4-carboxylic acid metabolite (CL 99,900), and 79.6% as unidentified. In order to characterize the unidentified compounds, extract aliquots were reacted with sodium hydroxide, hydrochloric acid, diazomethane, acetic anhydride in pyridine, and also subjected to diazotization followed by coupling using either β-naphthol or N-(1-naphthyl)ethylenediamine. The above chemical reactions, with the exception of diazomethane, affected the polar compounds, which suggested that aliphatic alcohols and aromatic amine functions were present. Note that ~89% of the total ^{14}C residues in or on hulls was unidentified (this includes 47% unextractable ^{14}C.

Zulalian et al. (1980, Report No. PD-M Vol. 16-30) conducted a metabolism study to determine the nature of the unidentified residues found in or on peanut hulls in the previous greenhouse study by Marei et al. (1975, PP# 6F1741). Field-grown peanut hulls were treated with a combination of [^{13}C]-pendimethalin labeled in the 3-methyl group and [^{14}C]pendimethalin labeled in the 3- and 4-methyl groups at 0.75 lb ai/A as a preplant incorporation (involved two field experiments). Also, greenhouse-grown peanut hulls were treated with [^{14}C]pendimethalin (labeled in the 4-methyl position) as a preplant incorporation or [^{14}C]pendimethalin (labeled in the 3- and 4-methyl groups) as a postemergence incorporation. Samples of peanut hulls collected at harvest were either extracted twice with methanol using a homogenizer and analyzed by TLC-autoradiography as in the study performed by Marei et al. followed by extraction with 2% HCl in methanol or rinsed with methanol to remove surface residues and extracted twice with 2% HCl in methanol using a homogenizer. Methanol rinses and extracts were analyzed by LSC (unextractable residues were combusted) and TLC using four different two dimensional solvent systems which were: (i) xylene:chloroform:methanol (200:50:5) vs. 1,2-dichloroethylene (cis-trans mixture):carbon tetrachloride:nitromethane (150:50:50); (ii) methylene chloride:methanol (225:75) vs. benzene:dioxane:-acetic acid (270:90:3); (iii) chloroform:methanol:water (225:66:9) vs. chloroform:acetone:acetic acid (180:90:30); and (iv) ethyl acetate:n-propanol:formic acid:water (120:200:20:60) vs. ethyl acetate:n-propanol:ammonium hydroxide:water (120:200:20:60). The acid methanol extracts from peanut hulls were partitioned between chloroform and water in order to isolate organosoluble metabolites and both fractions were analyzed by TLC. Extracts were also subjected to reactions with the following chemicals: 10% hydrochloric acid (acid hydrolysis), acetic anhydride and triethylamine (acetylation), and diazomethane (methylation). The acid methanol and methanol extracts from some field-grown hull samples were concentrated to remove the methanol, partitioned between methylene chloride and water, and analyzed by LSC and TLC; both fractions were then subjected to hydrolysis, TLC analysis again, and then extracted with methylene chloride three times before a final TLC and LSC analysis. Water-soluble radioactivity was analyzed by high-pressure liquid chromatography (HPLC) using water:methanol (80:20 and 20:80) and LSC. A GC/MS spectrometer was also employed for metabolite identification.

Total residues of radioactivity (pendimethalin equivalents) in or on peanut hulls from one field experiment (involved two replicates) were 5.25 ppm (includes 0.13 ppm in the methanol rinse, 3.98 ppm as acid-methanol-extractable, and 1.14 ppm as unextractable) and 4.96 ppm (includes 1.63 ppm as methanol-extractable, 1.79 ppm as acid-methanol-extractble, and 1.54 ppm as unextractable). In the second field experiment, radioactive residue levels in or on hulls were at only 0.43 ppm (includes 0.03 ppm in the methanol rinse, 0.31 ppm as acid-methanol-extractable, and 0.09 ppm as unextractable); harvested peanuts were severely damaged in this experiment because of large amounts of rainfall. From the greenhouse experiments, total radioactive residues were at 1.21-2.48 ppm (includes 0.54-1.25 ppm as methanol-extractable, 0.26-0.70 ppm as acid-methanol-extractable, and 0.41-0.53 ppm as unextractable) as the result of the preplant treatment and were at 7.21 ppm (includes 0.55 ppm from the methanol rinse, 5.34 ppm as acid-methanol-extractable, and 1.32 ppm as unextractable) and 8.4 ppm (includes 2.77 ppm as methanol-extractable, 3.48 ppm as acid-methanol-extractable, and 2.15 ppm as unextractble) as the result of the postemergence treatment. Acid hydrolysis of both methylene chloride and water fractions partitioned from the methanol and acid-methanol extracts containing 3.42 ppm of radioactive residues (second field experiment mentioned) resulted in 0.69 ppm of pendimethalin-related compounds being identified as pendimethalin itself at 0.08 ppm, CL 202,347 at 0.07 ppm, CL 217,146 at 0.24 ppm, CL 113,072 at 0.15 ppm, and other compounds (identity unspecified) combined at 0.15 ppm; this accounts for 20% of the radioactivity found in the combined methanol and acid methanol extracts (3.42 ppm) and only 14% of the total radioactivity (4.96 ppm) in the peanut hulls. The aqueous portion of this analysis accounted for 48% (1.63 ppm) of the total radioactive residues in the peanut hulls and was evaluated by HPLC with UV detection which showed many UV absorbing compounds and 10 or more carbon-14 compounds in trace amounts; unfortunately, the amounts of the radioactive compounds were too low to permit identification. Approximately 15% of the extractable radioactivity was unidentified (very polar) and did not correspond to any of the 55 compounds that were synthesized as pendimethalin-related (containing the pendimethalin moiety). The methanol extract alone of the field-grown peanut hulls described above contained 1.63 ppm of radioactivity (accounts for 33% of the total radioactivity present) which was

shown by TLC analysis to consist of 2.7% pendimethalin, 2.7% CL 202,347, <0.1% CL 217,146, 0.9% CL 99,900, 0.7% CL 113,066, 0.9% CL 113,067, 4% CL 113,068, 0.3% CL 113,071, and 1.4% CL 113,072. Whereas only a trace amount (<0.1%) of the CL 217,146 metabolite was found in the methanol extract, a greater amount (unspecified concentration) was observed in the subsequent acid-methanol extract which suggested that it had been released from a conjugate. Unidentified compounds (quantitation not performed) in the chloroform fraction from the acid-methanol extract (67% of the radioactivity partitioned into the chloroform phase) from the greenhouse postemergence study were found to react with diazomethane (the metabolites CL 99,900 and CL 113,072 also were found to react with this chemical and be converted to less polar compounds) and with acetic anhydride and triethylamine (suggests the presence of free hydroxy or amino functional groups) which converted all of the radiospots to less polar compounds. After an acid-hydrolysis experiment, two new radiospots were formed, both of which were found to react with diazomethane; it was suggested that these products from hydrolysis could, therefore, be carboxylic acids although no direct evidence was provided of this. TLC analysis of the hydrolysis products identified the metabolites CL 113,071 and CL 113,072. The metabolite CL 113,072 appeared as the major hydrolysis product and the authors indicated that some of the metabolites found in peanut hulls were conjugates of this compound. This study offered the most complete attempt to identify radioactive residues of pendimethalin and did suggest that some of the unidentified radioactive residues encountered were not pendimethalin-related compounds. No attempt was made to identify the residues contained in the unextractable portion of the hulls.

Oliver (1978, MRID No. 00058478) submitted information on a study involving the nature of radioactive residues in soybean plants grown (to maturity) in soil treated with 100 ppb of [^{14}C]N-nitrosopendimethalin. Plant samples were extracted with ethyl acetate and then with methanol using a homogenizer. Combustion analysis was used to determine total ^{14}C and TLC was used to identify the radioactive residues present. Soybean lower leaves were found to contain 9.8 ppb of radioactivity (21% was extractable); root samples contained 59 ppb of radioactivity (33% was extractable); lower stem samples contained 14 ppb of radioactivity (25% was extractable). Comparison of R_f values of a

standard and the extracted material, detected no levels of N-nitrosopendimethalin in any of the samples. This experimental summary is presented for general information purposes because nitrosoamines are contaminants of pendimethalin formulations.

A complete report of this experiment, including the raw data, was not available.

In summary, the available plant metabolism data do demonstrate that pendimethalin residues are absorbed and translocated by plants; however, we believe the available data to be inadequate because significant fractions of the extractable radioactive residues found in plants (for example: 42% in red table beet plants, 67% in cotton plants, 87-89% in wheat plants, and 40% in rice plants) could not be identified; 42-89% of total ^{14}C residues were unidentified. The most complete attempt at characterization of residues was performed in a study involving peanut hulls; however, only 14% of the total ^{14}C residues were identified and we do not feel that this is a representative commodity especially since hulls may have absorbed/adsorbed soil residues. Furthermore, radioactive residues unextractable from plant material were not characterized and this often constituted a significant percentage of the total radioactivity present (for example: 33% in red table beets and sweet corn, 50% in soybean plants and pods, and 18-53% in peanut hulls). Therefore, additional plant metabolism data are needed to reveal the complete identity of radioactive extractable and nonextractable residues that are encountered in representative plant tissues as the result of treatment with radiolabeled pendimethalin. Unidentified extractable radioactivity was usually associated with highly polar material which should be characterized in the requested data. In addition, we recommend that more rigorous acid, base, and/or enzymatic hydrolysis steps be included in the experimental methodology because the data submitted did suggest that pendimethalin metabolites are released by hydrolysis from possible conjugates. In some of the studies submitted, the unknown polar compounds were reacted with diazomethane and a response did or did not occur; pendimethalin-related compounds would be expected to react with this chemical because they bear hydroxy and/or carboxylic acid groups. In the requested data, further characterization beyond this step should be performed (i.e., identify pendimethalin-related

compounds via GC, MS, and/or HPLC or show that radioactivity has undergone natural-incorporation into plant tissues). In plants, pendimethalin appears to undergo degradation presumably as it does in animals and soil, through oxidation of alkyl groups (4-methyl [benzene ring] and N-1-ethylpropyl [amine moiety] groups) to form alcohols and carboxylic acids as well as hydrolytic cleavage of the N-ethylpropyl group. The registrant must determine the levels of metabolites remaining unextractable in plant tissues and in polar fractions because relative amounts must be known so that the Toxicology Branch may determine if these are additional residues of concern.

NATURE OF THE RESIDUE IN ANIMALS

Conclusions:

Presently, the metabolism of pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] (CL 92,553) in animals is not adequately understood because the available ruminant study did not identify residues in tissues or milk and because large amounts of radioactivity were not characterized in rat tissues (particularly kidney and liver). Thus, the residues of concern in food animals and their products cannot be ascertained. The following data are required:

- Metabolism studies utilizing ruminants. Animals must be dosed with ring-labeled [^{14}C]pendimethalin for 3 days at a level (>1.5 ppm) sufficient to make residue identification possible. Animals must be sacrificed within 24 hours of the final dose. The distribution and characterization of residues must be determined in milk, muscle, fat, kidney, and liver. If ruminant metabolism is found to differ significantly from that in rats, then swine metabolism data will also be required.

Presently the poultry feed items do not contain any detectable residues of pendimethalin and its metabolite (CL 202.347) (<0.05 ppm each). Accordingly the metabolism of these residues in poultry are of little concern. However if the additional requested plant-metabolism studies indicate the presence of other detectable metabolites of concern, then metabolism studies for poultry may be needed.

The following metabolites of pendimethalin (CL 92,553) have been identified in the tissues and urine of rats: the parent (CL 92,553), 4-[(1-ethylpropyl)-amino]-2-methyl-3,5-dinitrobenzyl alcohol (CL 202,347), 4-[(1-ethylpropyl)-amino]-3,5-dinitro-o-toluic acid (CL 99,900), 3-(2,6-dinitro-3,4-xylidino-2-pentanol (CL 113,066), 4-[[(1-carboxymethyl)propyl]amino]-3,5-dinitro-o-toluic acid (CL 113,071), and 4-[(1-ethyl-2-hydroxypropyl)amino]-3,5-dinitro-o-toluic acid (CL 113,072). Two additional metabolites, 4-amino-3,5-dinitro-

o-toluic acid (CL 202,078) and 4-[(1-ethyl-3-hydroxypropyl)amino]-3,5-dinitro-o-toluic acid (CL 202,345) have also been identified in rat urine, but not in rat tissues. In addition, pendimethalin per se and CL 202,347 have been identified in goat urine and fish tissues. Refer to Table 1 (see Nature of the Residue in Plants section) for structures of these metabolites. (p. 3).

References (used):

Haugwitz, M.I., and Eisner, S.K. 1974. PROWL® herbicide: Residual activity in lactating goats treated with ^{14}C-CL 92,553 [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitro-benzenamine]. Unpublished study received Aug. 25, 1980 under 241-243. Submitted by American Cyanamid Co. (CDL:099565-F; MRID:00067288).

Goldhamer, R.E. 1973. Metabolism of ^{14}C-CL 92,553 administered in capsules to lactating goats: Experiment Reference No. A-987; PD-M 11:233-244. Unpublished study received Aug. 25, 1980 under 241-243. Prepared by Biometric Testing, Inc., submitted by American Cyanamid Co. (CDL:099565-G; MRID:00067-289).

Kapoor, I.P. 1974. PROWL® herbicide: Metabolism X. Isolation, identification, and characterization of CL 92,553 and its metabolites in fish and its aquatic environment. Exhibit 43, Section H. Submitted by American Cyanamid Co. under PP#5G1567. (Unknown accession number; no MRID assigned).

Zulalian, J. 1973. CL 92,553: Metabolism III. Isolation and identification of metabolites present in urine, feces, and selected tissues of rats treated with carbon-14 CL 92,553 [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine], PROWL® herbicide. Exhibit 46, Section H. Submitted by American Cyanamid Co. under PP#5G1567. (Unknown accession number; no MRID assigned).

Analytical Bio Chemistry Laboratories, Inc. 1980. Residue accumulation study in crayfish (Procambarus simulans) with ^{14}C-CL 92,553 (pendimethalin) under static conditions. Prepared for and submitted by American Cyanamid Co. under PP#0F2401(099889). (No MRID assigned).

Discussion of the data:

American Cyanamid Co. [MRID:00067288 (CDL:099565-F)] submitted a study pertaining to the metabolism of pendimethalin in lactating goats; the experimental dosing and handling of these animals was conducted by Biometric Testing, Inc. [MRID:00067289 (CDL:099565-G)]. Lactating goats (one/dose group) received [^{14}C]pendimethalin labeled in the 4-methyl group of the molecule via capsule for 10 days at 0.5 ppm (0.013 mg/kg), 1.5 ppm (0.040 mg/kg), or 20 ppm (0.540 mg/kg); mg/kg body weight given parenthetically. Total residues of [^{14}C]pendimethalin equivalents were monitored daily in milk, urine, feces, and blood. The goats were slaughtered 2 hours after the last dose. At all dosage levels, the majority of ^{14}C ingested was excreted via the feces (54.3-66.6%); an additional 9.7-10.1% was excreted in the urine, 3.5-12.8% was present in rumen contents, 4.3-5.6% in intestinal contents, and <0.1% of the dose was accounted for in tissues, milk, and blood. Total [^{14}C]pendimethalin equivalents in milk from the goat treated at 20 ppm were 0.01 ppm after the third day of treatment. Total [^{14}C]pendimethalin equivalents were <0.01 ppm in leg and tenderloin muscle, brain, and back fat from all dosage levels. At the 0.5 ppm feeding level, total ^{14}C residues were 0.03 ppm in liver, 0.01 ppm in kidney, and <0.01 ppm in heart and omental fat. At the 1.5 ppm feeding level, total ^{14}C residues were 0.04 ppm in liver and kidney, 0.01 ppm in omental fat, and <0.01 ppm in heart. At the 20 ppm feeding level, total ^{14}C residues were 0.25 ppm in liver, 0.09 ppm in kidney, 0.01 ppm in heart, and 0.03 ppm in omental fat. Six-day urine samples were partitioned with ethyl acetate and 30% of the administered radioactivity was recovered in the organosoluble fraction. Identification of CL 202,347 and two unidentified metabolites in urine was achieved by two dimensional TLC using three different solvent systems; residues of pendimethalin per se plus eight unidentified metabolites were detected in 6-day fecal samples. Residues in milk and tissues were not characterized.

American Cyanamid Co. [PP# 5G1567 (accession no. unknown)] submitted a study conducted by Bionomics, E.G. & G., Inc. pertaining to the metabolism of pendimethalin in catfish. Bionomics conducted the experimental exposure of the catfish and elucidated the distribution and persistence of [^{14}C]pendimethalin

in soil, water and fish; characterization of these residues in fish tissues was undertaken by American Cyanamid Co. A static, laboratory-simulated aquatic system containing soil treated with ^{14}C ring-labeled pendimethalin at a theoretical soil concentration of 7.8 mg/kg (~2 lb ai/A) was stocked with 125 catfish (Ictalurus punctatus, average individual weight 4.4 g); the method of calculation of the lb ai/A rate was unspecified. Water, soil, and fish samples were removed at regular intervals during the 42-day treatment period. Analysis of water samples for total radioactivity was by liquid scintillation counting (LSC); soil and fish samples were combusted prior to LSC. On the first day of exposure, residues of [^{14}C]pendimethalin equivalents were 2.65 ppm in edible muscle and 5.77 ppm in viscera of fish removed from water containing 0.004 ppm ^{14}C residues. Total ^{14}C residues reached a maximum of 15.91 ppm in edible muscle after 14 days (viscera contained 20.0 ppm); water sampled at the same interval contained 0.011 ppm. Total ^{14}C residues steadily declined in fish tissues and increased in water during the remaining sampling intervals; after 42 days, ^{14}C pendimethalin residues were 0.73 ppm in edible muscle, 3.36 ppm in viscera, and 0.014 in water. Upon depuration, total ^{14}C residues (pendimethalin equivalents) in muscle declined to 0.28 ppm after 7 days and 0.07 ppm after 14 days. This indicates a fairly rapid loss of residues from tissues. Analysis of soil samples showed that ^{14}C residues remained fairly constant (5.13-9.23 ppm, average of 6.83 ppm) during the 42-day treatment period. Edible muscle from fish (five samples) taken at the 28-day sample interval was extracted with acetonitrile and 96% of the ^{14}C was recovered. TLC (two-dimensional) indicated that 93% of the radiolabeled material extracted from fish muscle was pendimethalin per se, 2% was the metabolite CL 202,347, and 5% was unidentified.

American Cyanamid Co. [PP#0F2401(099889)] submitted a study conducted by Analytical Bio Chemistry Laboratories, Inc. in which 65 crayfish (Procambarus simulans, average individual weight 8.1 g) were placed in a static, laboratorysimulated aquatic system containing soil treated with [^{14}C]pendimethalin at a level equivalent to 1 lb ai/A (10 mg [^{14}C]pendimethalin in 10 kg soil). Note: the computation method used to obtain this field application rate was not provided. Water samples were analyzed for total radioactivity by LSC and analysis of crayfish samples was performed by combustion/LSC. After 1 day,

residues of [^{14}C]pendimethalin equivalents were 0.21 ppm in six whole crayfish removed from water containing 0.014 ppm ^{14}C equivalents; in 12 additional crayfish, the edible portions (abdominal muscle) contained 0.026 ppm and inedible portions (pincers, carapace, walking legs, exoskeleton, and letson) contained 0.26 ppm. Total ^{14}C residues reached a maximum after 7 days of exposure: 0.39 ppm in whole crayfish, 0.071 in edible portions, and 0.48 ppm in inedible portions of crayfish removed from water containing 0.026 ppm [^{14}C]pendimethalin equivalents. After 14 days, total ^{14}C declined to 0.29 ppm in whole crayfish, 0.048 in edible portions, and 0.33 ppm in inedible portions sampled from water containing 0.032 ppm ^{14}C. Eighteen additional crayfish were transferred to pendimethalin-free water and, after a 7-day depuration period, ^{14}C residues were 0.16 ppm in whole crayfish and inedible portions, and 0.014 ppm in edible portions. These data indicate that residues are preferentially transferred to inedible crayfish tissues; only 12-18% of the ^{14}C residues detected in whole crayfish from all sample intervals were found in edible tissues. These data also show that residues do not accumulate substantially in any portion of crayfish tissues, particularly edible tissues, and that residues depurate rapidly. Residues of [^{14}C]pendimethalin were not characterized.

American Cyanamid Co. [PP#5G1567 (accession no. unknown)] submitted a study conducted by Zulalian (1973) in which an unspecified number of rats were dosed with 37 mg/kg of [^{14}C]pendimethalin labeled in the 4-methyl group on the benzene ring. Additional details on the method of administration, number of doses administered, and collection of samples were not provided with the exception that samples of urine, feces and tissues were obtained at 6-, 12-, 24-, and 48-hour intervals. At the 24-48 hour collection interval, 74.3% of the radioactivity had been eliminated in the feces and 20.1% had been eliminated in the urine. Six hours after dosing, total [^{14}C]pendimethalin equivalents were 29.8 ppm in liver, 16.9 ppm in kidney, 5.4 ppm in blood, 1.3 ppm in muscle, and 12.2 ppm in fat; 24 hours after dosing, levels decreased to 1.6 ppm in liver, 1.3 ppm in kidney, 0.4 ppm in blood, 0.2 ppm in muscles, and 4.9 ppm in fat. Identification of pendimethalin *per se* as the major residue component in the 12-hour fecal sample was accomplished by ethanol extraction (78% of the radioactivity was recovered) and two-dimensional TLC

against known standards; confirmation of pendimethalin was by MS and GC. Of the identified urinary residues, CL 113,072 accounted for 30% of the ^{14}C residues, CL 113,071 accounted for 14.4%, CL 99,900 accounted for 2.0%, CL 202,078 and CL 202,345 each accounted for 1.0%, and CL 113,066, CL 202,347 and pendimethalin (CL 92,553) each accounted for ≤0.4%; 50.6% of the ^{14}C residues were unidentified. The 6-12 hour samples of muscle, blood, kidney, and liver were extracted with ethanol; fat samples were extracted with benzene and further purified by partitioning between hexane and acetonitrile. Characterization of residues in these tissues was accomplished by cochromatography against known standards or synthesized model compounds. The predominant residues identified in the various tissues and their relative percentages (given in parentheses) are as follows: pendimethalin per se (28.5%), CL 99,900 (32.2%) and CL 113,072 (30.0%) in muscle; CL 99,900 (41.0%) and CL 113,072 (25.2%) in blood; and pendimethalin per se (80.9%) in fat. Small amounts of CL 202,347 (4.2%) and CL 99,900 (5.3%) were also found in fat. Total ^{14}C residues recovered from kidney and liver tissues with ethanol was 71% and 65%, respectively, but only a small portion of the recovered ^{14}C residues in these tissues were identified. In kidney, pendimethalin per se accounted for 8.8%, CL 99,900 accounted for 5.4%, and CL 113,072 accounted for 6.0%; trace amounts of pendimethalin, CL 99,900, and CL 202,347 were also chromatographically identified in liver. Unidentified compounds migrating and nonmigrating) accounted for 77.6% and 93.7% of the radioactivity in kidney and liver, respectively. When treated with diazomethane, residues from ethanol-extracted liver samples were converted to less polar metabolites. Based on this reaction, the author suggests that these metabolites are carboxylic acid derivatives of the parent (CL 92,553) although no direct evidence of this was provided.

The available data for rats indicate that ingested residues of pendimethalin are excreted via feces largely as the parent; residues are excreted via urine in the form of o-toluic acids (CL 99,900, CL 113,072, CL 113,071, CL 202,078, and CL 202,345) with various modifications of the N-alkyl side chain. Residues transferred to rat tissues largely as the parent (CL 92,553), CL 99,900 and CL 113,072; small amounts of CL 92,553, CL 99,900, and CL 202,347 were identified in liver and kidney but the majority of the extractable residues

remained unknown. These rat metabolism data are useful for comparative purposes but cannot be used to satisfy the metabolism data requirements for ruminants and poultry. We conclude that the metabolism of pendimethalin in animals has not been adequately described. Additional data are required for ruminants and possibly poultry; refer to Conclusions section for specific data gaps.

RESIDUE ANALYTICAL METHODS

Conclusions:

Acceptable GC methods are available for the collection of data pertaining to residues of pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] (CL 92,553) and its metabolite 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol (CL 202,347) in or on plant commodities or their processed products. In addition, GC methods are available for the quantification of pendimethalin per se in milk and fish, and of pendimethalin per se and its metabolite 4-[(1-ethylpropyl)amino]-3,5-dinitro-o-toluic acid (CL 99,900) in water. These GC methods are also adequate for tolerance enforcement. Four of the registrant-submitted methods are included as Methods I, II, III, and IV in PAM Vol. II. Refer to the Discussion of the data section for details.

Note: Additional metabolism studies are required. If these studies indicate the presence of new metabolites, then additional methodology may be required.

References (used):

American Cyanamid Company. 1974. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in cottonseed. Method M-476.1 dated June 6, 1974. Unpublished study received Feb. 13, 1980 under 241-243. (CDL:241781-R; MRID:00025831).

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American Cyanamid Co. 1975. Analyses for residues of PROWL herbicide in wheat and other crops. Compilation; unpublished study received Oct. 29, 1979 under 241-243. (CDL:241256-A; MRID:00106830). [Includes Method Nos. M-530, M-531, M-539.1, M-541, M-540, M-529, M-538, M-459.1, and M-517.]

American Cyanamid Company. 1976. Residues of PROWL herbicide in sorghum. Compilation; unpublished study received Jan. 6, 1978 under 241-EX-88. (CDL:096712-A; MRID:00106791). [Includes Method Nos. M-743, M-744, M-745, and M-746.]

American Cyanamid Company. 1976. Summary of residue analysis of PROWL in peas. Includes methods M-597.1 dated Dec. 6, 1976; M-693 dated July 20, 1976; M-742 dated Dec. 6, 1976 and M-694 dated July 20, 1976. Compilation; unpublished study received Feb. 8, 1977 under 241-243. (CDL:095797-A; MRID: 00070962).

American Cyanamid Co. 1979. Residues of PROWL herbicide. Compilation; unpublished study received Sep. 21, 1979 under 241-EX-95. (CDL:098994-A; MRID:00106808). [Includes Method Nos. M-485, M-486, M-528, and M-522.1.]

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American Cyanamid Co. 1980. Residue Report Nos. C-1639, C-1723, C-1724, C-1726, and C-1727 in Section D of PP#0F2373(242640). (No MRID assigned).

Bohn, W.R. 1974. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in soybean seed. Method M-533 dated Jul. 30, 1974. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-D; MRID:00025821).

Bohn, W.R. 1974. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in soybean seed. Method M-536 dated Aug. 6, 1974. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-K; MRID:00025827).

Boughton, P.J. 1974. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in cottonseed. Method M-523 dated May 24, 1974. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-X; MRID:00025837).

Boughton, P. 1974. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in cottonseed meal. Method M-524 dated Jun. 28, 1974. Unpublished study received Sep. 12, 1978 under 241-243; submitted by American Cyanamid Co. (CDL:235084-I; MRID:00019004).

Boughton, P.J. 1974. CL 92,553: Determination of N-(1-ethylpropyl-3,4-dimethyl-2,6-dinitrobenzenamine in cottonseed oil. Method M-514 dated May 24, 1974. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-S; MRID:00025832).

Boughton, P.J. 1974. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6 dinitrobenzenamine in cotton plants. Method M-516 dated June 5, 1974. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-T; MRID:00025833).

Boughton, P.J. 1974. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in soybean green seed. Method M-560 dated Nov. 12, 1974. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-E; MRID:00025822).

Boughton, P.J. 1974. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in soybean green seed. Method M-561 dated Nov. 12, 1974. Unpublished study received Nov. 20, 1975 under 6F1704; submitted by American Cyanamid Co. (CDL:094648-I; MRID:00041904).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in lima beans. Method No. M-607 dated June 9, 1975. Unpublished study received Feb. 9, 1976 under 6G1739; submitted by American Cyanamid Co. (CDL:095485-E; MRID:00039520).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in lima bean foliage and pods. Method No. M-608 dated June 9, 1975. Unpublished study received Feb. 9, 1976 under 6G1739; submitted by American Cyanamid Co. (CDL:095485-F; MRID:00052558).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in peanuts. Method M-577 dated Feb. 18, 1975. Unpublished study received Feb. 9, 1976 under 6G1740; submitted by American Cyanamid Co. (CDL:095393-C; MRID:00072822).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in peanut foliage, hay and hulls. Method M-578 dated Feb. 18, 1975. Unpublished study received Feb. 9, 1976 under 6G1740; submitted by American Cyanamid Co. (CDL:095393-D; MRID 00072823).

Boughton, P. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in peanut meal. Method M-592 dated Apr. 2, 1975. Unpublished study received Feb. 9, 1976 under 6G1740; submitted by American Cyanamid Co. (CDL:095393-F; MRID:00051960).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in peanut oil. Method M-590 dated Apr. 2, 1975. Unpublished study received Feb. 9, 1976 under 6G1740; submitted by American Cyanamid Co. (CDL:095393-E; MRID:00051959).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in potato vines. Method No. M-614 dated June 23, 1975. Unpublished study received Feb. 9, 1976 under 6G1739; submitted by American Cyanamid Co. (CDL:095485-M; MRID:00039527).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in soybean meal. Method M-604 dated Apr. 24, 1975. Unpublished study received Nov. 20, 1975 under 6F1704; submitted by American Cyanamid Co. (CDL:094648-F; MRID:00041901).

Boughton, P.J. 1975. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in soybean oil. Method M-602 dated Apr. 24, 1975. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-F; MRID:00024823).

Boughton, P.J. 1975. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in lima beans. Method No. M-609 dated June 9, 1975. Unpublished study received Feb. 9, 1976 under 6G1739; submitted by American Cyanamid Co. (CDL:095485-G; MRID:00039521).

Boughton, P.J. 1975. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in lima bean foliage and pods. Method No. M-610 dated June 9, 1975. Unpublished study received Feb. 9, 1976 under 6G1739; submitted by American Cyanamid Co. (CDL:095485-H; MRID:00039522).

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Boughton, P.J. 1975. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in peanut meal. Method M-593 dated Apr. 2, 1975. Unpublished study received Feb. 9, 1976 under 6G1740; submitted by American Cyanamid Co. (CDL:095393-J; MRID:00051962).

Boughton, P. 1975. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in peanut oil. Method M-591 dated Apr. 2, 1975. Unpublished study received Feb. 9, 1976 under 6G1740; submitted by American Cyanamid Co. (CDL:095393-I; MRID:00072825).

Boughton, P. 1975. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in potato tubers. Method No. M-615 dated June 23, 1975. Unpublished study received Feb. 9, 1976 under 6G1739; submitted by American Cyanamid Co. (CDL:095485-N; MRID:00039528).

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Boughton, P.J. 1975. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol in soybean meal. Method M-605 dated Apr. 24, 1975. Unpublished study received Nov. 20, 1975 under 6F1704; submitted by American Cyanamid Co. (CDL:094648-L; MRID:00072810).

Boughton, P. 1975. CL 202,347: Determination of 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitro benzyl alcohol in soybean oil. Method M-603 dated Apr. 24, 1975. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-M; MRID:00025828).

Boughton, P.J. 1975. PROWL® (CL 92,553): The gas chromatographic determination of CL 92,553...and CL 202,347...from fortified peanut tissues (foliage, hay, hulls and nuts) and processed commodities (oil and meal): Report No. C-655. Unpublished study received Feb. 9, 1976 under 6G1740; submitted by American Cyanamid Co. (CDL:095393-B; MRID:00051958).

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Boughton, P.J., Bohn, R., Tondreau, R.E. 1975. PROWL (CL 92,553): The gas chromatographic determination of CL 92,553 N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine and CL 202,347 4-(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol from fortified soybean tissues (foliage, green seeds

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Boughton, P.J., et al. 1976. PROWL® (CL 92,553): Validation of M-701, M-702, M-703, M-704, and M-705, M-706, M-707, M-708 for the determination of CL 92,-553 and CL 202,347 residues in sunflower seed, straw, meal, and oil. Report No. C-977, dated 7/16/76. Submitted by American Cyanamid Co. under PP#0F2373 (242640). (No MRID assigned).

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Smith, J. 1979. PROWL® pendimethalin (CL 92,553): Validation of GC method M-1029 for the determination of CL 217,146 and CL 202,347 residues in peanut hulls: Report No. C-1618. Includes method M-1029 dated Oct. 11, 1979. Unpublished study received Apr. 29, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:099395-C; MRID:00031214).

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Wyckoff, J.C. 19??. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in corn plants. Undated method M-458.1. Unpublished study received Sep. 17, 1974 under 5F1556; submitted by American Cyanamid Co. (CDL:094474-C; MRID:00023781).

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Wyckoff, J. 1974. CL 92,553: Determination of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine in corn grain. Undated method M-465.1. Unpublished study received Sep. 27, 1974 under 5F1556; submitted by American Cyanamid Co. (CDL:094474-E; MRID:00023782).

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Wyckoff, J.C., Tondreau, R.E. 1974. PROWL (CL 92,553): The gas chromatographic determination of CL 92,553...and CL 202,347...residues in corn (foliage), soybean (foliage), and wheat (foliage) and CL 92,553 in soil: Report No. C-454. Summary of studies 094474-C through 094474-E. Unpublished study received Sep. 27, 1974 under 5F1556; submitted by American Cyanamid Co. (CDL:094474-B; MRID:00023780).

Discussion of the data:

American Cyanamid Co. submitted separate procedures for the determination of pendimethalin per se and its metabolite 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol (CL 202,347) in various plant commodities and their processed products. The American Cyanamid Co. method designation numbers and corresponding references (MRID or petition number) for each commodity is presented in Tables 2 and 3. Specific procedures utilized to quantify pendimethalin per se and its metabolite in these commodities are discussed below in detail. In general, analytical methodology for all plant samples involves solvent extraction and the removal of coextractives by various solvent partitionings. The addition of a derivatization step is required for determination of CL 202,347. Final cleanup for both parent and metabolite is by adsorption chromatography on Florisil, and residue determination is accomplished by GC with a ^{63}Ni electron capture detection system against an external standard. American Cyanamid Co. methods M-483.1, M-560, M-602, M-533, and M-604 for determination of pendimethalin per se and methods M-531, M-561, M-603, M-536, and M-605 for determination of CL 202,347 in soybean samples are included in PAM Vol. II (Pesticide Reg. Sec. 180.361) as Methods I and II, respectively. Methods M-516, M-476.1, M-524, and M-514 determine pendimethalin per se and methods M-517, M-523, M-525, and M-515 determine CL 202,347 in cotton samples; respectively, they are Methods III and IV in PAM Vol. II (Pesticide Reg. Sec. 180.361). Methods I, II, III, and IV are essentially the same;

Methods II and IV require reaction with acetic anhydride for the determination of the metabolite CL 202,347. A method trial was conducted on M-516 and M-517 by the Analytical Methods and Special Investigations Section (EPA memorandum by W.J. Boodee dated 3/25/75; in correspondence file of PP#5F1556) on cotton. These methods prescribed a 180-cm borosilicate glass tube packed with 5% EGSS-X on 100-120 mesh Gas-Chrom Q coupled to a Hewlett-Packard gas chromatograph equipped with a ^{63}Ni electron capture detector. Difficulties with this column were encountered; 3-4 weeks of constant conditioning were required before satisfactory recoveries were obtained (recovery values were not reported). Substitution of a 3-foot borosilicate column packed with 5% OV-225 on 80-100 chromosorb W-HP and use of a Tritium electron capture detector yielded recoveries of 84-88% for pendimethalin per se and 76-92% for CL 202,347 from cotton foliage at fortification levels of 0.05-0.10 ppm.

American Cyanamid Co. submitted separate methods for the quantitation of pendimethalin per se and its metabolite (CL 202,347) in cottonseed oil, peanut oil, soybean oil, and sunflower oil (see Tables 2 and 3, hexane extraction procedure, for specific method designation numbers). Determination of pendimethalin per se is achieved by extraction with hexane, partitioning into acetonitrile, adsorption chromatography on Florisil (elution with hexane/benzene [80:20]), and determination by GC with a ^{63}Ni electron capture detector system. Residues of CL 202,347 are similarily extracted and partitioned with the addition of a derivatization step (acetic anhydride and pyridine). The acetyl derivative is then extracted into hexane; elution from the Florisil column is with benzene and determination is by ECGC, as above. Recoveries of pendimethalin per se and CL 202,347 following fortification of untreated oil samples at 0.05-1.0 ppm are listed in Table 2 and Table 3, respectively.

American Cyanamid Co. also submitted separate procedures which involve the chloroform-methanol extraction of pendimethalin per se and its metabolite (CL 202,347) from corn grain, cottonseed, cottonseed meal, dry lima beans, oat grain, dry peas, peanuts, peanut meal, sorghum grain, soybean seed, soybean meal, sunflower seed, sunflower meal, and wheat grain; the method for rice grain (M-444.1) determines the parent only (see Tables 2 and 3, chloroform-methanol extraction procedure, for specific method designation numbers).

Determination of pendimethalin per se in these commodities entails extraction with chloroform-methanol, a hexane-acetonitrile partitioning step and/or adsorption chromatography on Florisil, and determination by GC with a ^{63}Ni electron capture detection system. Similar extraction and liquid partitioning procedures are employed to determine residues of CL 202,347; a derivatization step (acetic anhydride and pyridine) is added so that the metabolite is determined as its acetyl derivative. A modification of these procedures is prescribed for cottonseed meal in M-524 and M-525: following extraction, residues are taken up with hexane and a 2-minute centrifugation step is added prior to the Florisil cleanup. In addition to data pertaining to recoveries of pendimethalin per se and CL 202,347 following fortification of untreated seed, grain, and meal samples at 0.05-5.0 ppm (see Tables 2 and 3), American Cyanamid Co. (MRID:00051958, Report No. 655) also submitted extraction efficiency data which showed that 83% of the field-applied [^{14}C]pendimethalin (0.75 lb ai/A) was recovered from peanut nutmeats following a single chloroform-methanol extraction.

Two general procedures, both involving an aqueous acidic methanol extraction step, were submitted by American Cyanamid Co. for the determination of pendimethalin per se and CL 202,347 in beet foliage and roots, corn foliage and fodder, cotton foliage, lima bean foliage and pods, oat foliage and straw, peanut foliage, peanut hay and hulls, peas, pea pods and pea vines, potato tubers and vines, sorghum forage and fodder, soybean green seed and foliage, sunflower straw, and wheat foliage and straw; the method for rice straw (M-444.1) determines the parent only (see Tables 2 and 3, aqueous acidic methanol extraction procedure, for specific method designation numbers). Determination of pendimethalin per se in each of these commodities is achieved by extraction with aqueous acidic-methanol, liquid partition into hexane, or hexane-acetonitrile in the case of cotton foliage (M-516), sunflower straw (M-702), and peanut foliage, hay and hulls (M-578), adsorption chromatography on Florisil (elution with hexane-benzene), and determination by GC with a ^{63}Ni electron capture detection system. Residues of CL 202,347 are also extracted with aqueous acidic-methanol. A hexane partition is employed for beet roots and foliage (M-530), wheat foliage and straw (M-522.1), and corn foliage and fodder (M-459.1) and a hexane-acetonitrile partition is used for

sunflower straw (M-706) and peanut foliage, hay and hulls (M-580). Acidic methanol-extracted residues from the remaining commodities are partitioned into chloroform. Final cleanup prescribed by all methods employing acidic methanol extraction is on Florisil and determination is by GC, as above. The recoveries obtained using these methods are listed in Tables 2 and 3. In addition, American Cyanamid Co. submitted extraction efficiency data pertaining to the recovery of [^{14}C]pendimethalin from field-treated crops following a single extraction with aqueous acidic methanol. Radiolabeled pendimethalin was field-applied at 0.75-1.5 lb ai/A (unspecified formulation). After 40-360 days, recovery of the initial dose was 65-75% from corn foliage (MRID: 00023780, Report C-454), 67% from peanut foliage and 58% from peanut hulls (MRID:00051958, Report C-655), 62-73% from cotton foliage (MRID:00106752, Report No. C-481), 83% from beet foliage and 85% from beet roots (MRID:00106-830, Report C-499), and 67-72% from wheat foliage (MRID:00106830, Report C-590). Modifications of M-706 (M-706-AFID) for detection of CL 202,347 in sunflower plants involved use of an ID column (6 foot x 2 mm) packed with 3% OV-17 Gas Chrom Q and an AFID (alkali flame ionization detector) detector. The claimed method sensitivity is 0.05 ppm; control samples yielded values of <0.05 ppm but no recovery data were submitted.

These GC methods permit the quantitative determination of pendimethalin per se and its metabolite (CL 202,347) in or on plant commodities; they are considered adequate for purposes of data collection and tolerance enforcement. Control sample data were submitted for each method listed in Tables 2 and 3; control values for all commodities were <0.05 ppm (method sensitivity).

The confirmatory method submitted by American Cyanamid Co. [MRID:00023785, M-549] was tested on a single commodity (corn plants) and is applicable only to pendimethalin per se. Following aqueous acidic methanol extraction, the residue sample is partitioned into hexane and cleaned up on Florisil. The column eluate is then reacted with 10 N sodium hydroxide. The production of a violet-color indicates the presence of pendimethalin; other nitroanilides reportedly do not interfere. This method is not adequate for confirmation because 1) it does not indicate the presence of the metabolite CL 202,347 and 2) no indication of specificity was provided.

The optional use of different GC columns and detection systems provides the regulatory methodology with adequate confirmatory capability.

In addition to the GC methods for determination of pendimethalin per se and its CL 202,347 metabolite in or on peanut hulls, American Cyanamid Co. MRID: 00031214) submitted M-1029 which determines metabolites CL 202,347 and CL 217,146 in the same commodity. M-1029 is essentially the same as the previously-described M-580 which determines only CL 202,347 in peanut hulls. The methods differ in that M-1029 employs external standards of CL 202,347 and CL 217,146 and a 3% OV-225 column packing whereas M-580 uses a 5% EGSS-X column packing. Recoveries of CL 202,347 were 78.8% (0.1 ppm fortification) and recoveries of CL 217,146 were 81.9-107.5% following fortification of peanut hulls at 0.1-2.0 ppm. The GC method for detection of CL 217,146 in or on peanut hulls is considered adequate for data collection and tolerance enforcement. However, although the presently established tolerance for peanut hulls includes combined residues of pendimethalin per se, CL 202,347 and CL 217,146, the CL 217,146 metabolite is not considered toxicologically significant (see EPA memorandum by A. Smith, dated 4/2/81; in correspondence file for PP#6F1741). We recommend at this time that the present regulation for peanut hulls [40 CFR 180.361(b)] be deleted; peanut hulls should be included with other commodities for which tolerances were established for combined residues of pendimethalin per se and its CL 202,347 metabolite unless the requested plant metabolism studies reveal that CL 217,146 is indeed a residue of concern.

In addition to the methods for quantitation of pendimethalin per se and its metabolite (CL 202,347) in plant commodities, American Cyanamid Co. also submitted methods which determine pendimethalin per se in milk [Report No. C-384, Method No. M-461 (MRID:00023796)], fish [Report No. C-795, Method No. M-632 (MRID:00058835)], and water [Report No. C-757, Method M-631; PP#0F2401 (099889)]. Residues of pendimethalin per se are extracted from milk samples with methanol, from fish samples (whole fish, fillet, tail, and viscera) with acetonitrile, and from water samples with hexane. Cleanup is achieved by partitioning into hexane and/or adsorption chromatography on Florisil. Residues in fish and water samples are determined by GC with a ^{63}Ni electron capture detection system (5% EGSS-X on Gas Chrom Q, 100/120 mesh); residue quantitation in milk samples is by GC with a ^{63}Ni or Tritium electron source (3% OV-225 on Gas Chrom Q 60/80 mesh). Recoveries of pendimethalin per se from

milk were 82.6-97.7% at fortification levels of 0.01-0.50 ppm; recoveries from water samples were 94.2-114.3% at fortification levels of 0.005-0.030 ppm. Recoveries of pendimethalin per se were 88.9-125.7% from whole fish (0.05-10.0 ppm), 88.3-120.6% from viscera, 91.2-116.9% from fillet and tail (0.05-1.0 ppm), 129.4-136.5% from eggs, and 126.9-127.6% from testes (0.05-0.01 ppm); fortification levels given parenthetically.

American Cyanamid Co. [PP#0F2401(099889); Report No. C-1791, Method No. M-1113] also submitted a GC method which determines the pendimethalin metabolite [4-(1-ethylpropyl)amino]-3,5-dinitro-o-toluic acid (CL 99,900) in water. Water samples are acidified with HCl and extracted into methylene chloride. Following rotary evaporation, residues are taken up with acetone and methylated with diazomethane. The methyl ester of CL 99,900 is quantified by GC with a ^{63}Ni electron capture system. Recoveries of CL 99,900 were 82.1-117.7% at fortification levels of 0.001-0.005 ppm. The sensitivity of this method is 0.001 ppm. This metabolite is currently not regulated nor are pendimethalin residues regulated in water at this time.

Additional metabolism studies are required. If these studies indicate the presence of new metabolites, then additional methodology may be requried.

Table 2. Pendimethalin per se (CL 92,553) recovery data obtained from plant commodities (and processed products) using methods developed by American Cyanamid Co.

Commodity (grouped by extraction procedure)	Method reference (MRID or Petition No.)	Method No.	Fortification (ppm)	Percent recovery	Recovery data reference (MRID or Petition No.)
Hexane					
cottonseed oil	MRID 00025832	M-514	0.05-1.0	80.4-114.8	MRID 00106752
peanut oil	MRID 00051959	M-590	0.05-1.0	80.3-112.0	MRID 00051958
soybean oil	MRID 00025823	M-602	0.05-1.0	87.5-122.6	MRID 00041898
sunflower oil	PP#0F2373(242640)	M-704	0.05-1.0	88-102	PP#0F2373(242640)
Chloroform/Methanol					
corn grain	MRID 00023782	M-465.1	0.05-1.0	75.6-117.2	MRID 00023780
cottonseed	MRID 00025831	M-476.1	0.05-1.0	81.2-106.9	MRID 00106752
cottonseed meal	MRID 00019004	M-524	0.05-0.50	76.0-101.2	MRID 00106752
lima beans (dry)	MRID 00039520	M-607	0.05-1.0	87.8-131.9	MRID 00039519
oat grain	MRID 00106830	M-540	0.05-1.0	90.5-115.6	MRID 00106830
peas (dry)	MRID 00070962	M-693	0.05-5.0	78-118	MRID 00070962
peanut nutmeats	MRID 00072822	M-577	0.05-1.0	84.2-118.4	MRID 00051958
peanut meal	MRID 00051960	M-592	0.05-1.0	93.2-131.7	MRID 00051958
rice grain	MRID 00071120	M-444.1	0.05-1.0	86.8-114.8	MRID 00071120
sorghum grain	MRID 00106791	M-744	0.05-5.0	84.0-128.0	MRID 00106791
soybean seed	MRID 00025821	M-533	0.05-1.0	78.9-126.3	MRID 00041898
soybean meal	MRID 00041901	M-604	0.05-1.0	102.5-123.9	MRID 00041898
sunflower seed	PP#0F2373(242640)	M-701	0.05-5.0	79-121	PP#0F2373(242640)
sunflower meal	PP#0F2373(242640)	M-703	0.05-5.0	81- 98	PP#0F2373(242640)
wheat grain	MRID 00106808	M-486	0.05-1.0	91.5-110.9	MRID 00106830
Aqueous Acidic Methanol					
beets, foliage	MRID 00106830	M-529	0.05-0.50	75.3- 89.3	MRID 00106830
beets, roots	MRID 00106830	M-529	0.05-1.0	93.6-142.0	MRID 00106830
corn foliage and fodder	MRID 00023781	M-458.1	0.05-1.0	87.5-126.7	MRID 00023780
cotton foliage	MRID 00025833	M-516	0.05-1.0	72.1- 90.1	MRID 00106752

Commodity (grouped by extraction procedure)	Method reference (MRID or Petition No.)	Method No.	Fortification (ppm)	Percent recovery	Recovery data reference (MRID or Petition No.)
lima bean foliage	MRID 00052558	M-608	0.05-1.0	83.6-136.8	MRID 00039519
lima bean pods	MRID 00052558	M-608	0.05-1.0	96.6-136.0	MRID 00039519
oats, foliage	MRID 00106830	M-538	0.05-1.0	88.9-119.3	MRID 00106830
oats, straw	MRID 00106830	M-538	0.05-1.0	84.3-117.0	MRID 00106830
peanut foliage	MRID 00072823	M-578	0.05-1.0	80.0-117.1	MRID 00051958
peanut hay	MRID 00072823	M-578	0.05-1.0	72.0-112.5	MRID 00051958
peanut hulls	MRID 00072823	M-578	0.05-1.0	76.3-130.4	MRID 00051958
peas	MRID 00070962	M-597.1	0.05-1.0	91.7-103.0	MRID 00070962
pea pods	MRID 00070962	M-597.1	0.05-1.0	89.5-128.1	MRID 00070962
pea vines	MRID 00070962	M-597.1	0.05-5.0	73-126	MRID 00070962
potato tubers	MRID 00039526	M-613	0.05-1.0	86.0-109.1	MRID 00039526
potato vines	MRID 00039527	M-614	0.05-1.0	85.7-108.4	MRID 00039526
rice straw	MRID 00071120	M-444.1	0.05-1.0	84.0-118.2	MRID 00071120
sorghum forage	MRID 00106791	M-743	0.05-5.0	74.0- 95.0	MRID 00106791
sorghum fodder	MRID 00106791	M-743	0.05-5.0	73.0- 99.0	MRID 00106791
soybean foliage	MRID 00025820	M-483.1	0.05-5.0	95.2-110.1	MRID 00041898
soybean green seed	MRID 00025822	M-560	0.05-1.0	73.6-111.2	MRID 00041898
sunflower straw	PP#0F2373(242640)	M-702	0.05-5.0	84-114	PP#0F2373(242640)
wheat foliage	MRID 00106808	M-485	0.05-1.0	76.4-133.7	MRID 00106830
wheat straw	MRID 00106808	M-485	0.05-1.0	74.9-114.8	MRID 00106830

Table 3. CL 202,347 (4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol recovery data obtained from plant commodities (and processed products) using methods developed by American Cyanamid Co.

Commodity (grouped by extraction procedure)	Method reference (MRID or Petition No.)	Method No.	Fortification (ppm)	Percent recovery	Recovery data reference (MRID or Petition No.)
Hexane					
cottonseed oil	MRID 00106752	M-515	0.05-1.0	84.4-121.5	MRID 00106752
peanut oil	MRID 00072825	M-591	0.05-1.0	80.6-113.4	MRID 00051958
soybean oil	MRID 00025828	M-603	0.05-1.0	72.8- 90.8	MRID 00041898
sunflower oil	PP#0F2373(242640)	M-708	0.05-1.0	64-101	PP#0F2373(242640)
Chloroform/Methanol					
corn grain	MRID 00029020	M-466	0.05-1.0	79.7-114.2	MRID 00023780
cottonseed	MRID 00025837	M-523	0.05-1.0	43.2-140.0	MRID 00106752
cottonseed meal	MRID 00106752	M-525	0.05-0.50	82.0-128.7	MRID 00106752
lima beans (dry)	MRID 00039521	M-609	0.05-1.0	68.6- 93.2	MRID 00039519
oat grain	MRID 00106830	M-541	0.05-1.0	76.1- 96.8	MRID 00106830
peas (dry)	MRID 00070962	M-694	0.05-5.0	74-110	MRID 00070962
peanut nutmeats	MRID 00072824	M-579	0.05-1.0	85.5-115.1	MRID 00051958
peanut meal	MRID 00051962	M-593	0.05-1.0	84.2-102.9	MRID 00051958
sorghum grain	MRID 00106791	M-746	0.05-5.0	85.0-120.0	MRID 00106791
soybean seed	MRID 00025827	M-536	0.05-1.0	87.3-120.5	MRID 00041898
soybean meal	MRID 00072810	M-605	0.05-1.0	72.4- 94.1	MRID 00041898
sunflower seed	PP#0F2373(242640)	M-705	0.05-5.0	71-118	PP#0F2373(242640)
sunflower meal	PP#0F2373(242640)	M-707	0.05-5.0	74-116	PP#0F2373(242640)
wheat grain	MRID 00106808	M-528	0.05-1.0	100.2-119.8	MRID 00106830
Aqueous Acidic Methanol					
beets, foliage	MRID 00106830	M-530	0.05-0.50	73.1-119.4	MRID 00106830
beets, roots	MRID 00106830	M-530	0.05-0.50	90.3-100.8	MRID 00106830
corn foliage and fodder	MRID 00106830	M-459.1	0.05-1.0	75.2-110.8	MRID 00023780
cotton foliage	MRID 00106830	M-517	0.05-1.0	75.4-138.6	MRID 00106752
lima bean foliage	MRID 00039522	M-610	0.05-1.0	63.8- 98.5	MRID 00039519

Commodity (grouped by extraction procedure)	Method reference (MRID or Petition No.)	Method No.	Fortification (ppm)	Percent recovery	Recovery data reference (MRID or Petition No.)
lima bean pods	MRID 00039522	M-610	0.05-1.0	74.6- 92.5	MRID 00039519
oats, foliage	MRID 00106830	M-539.1	0.05-1.0	69.9- 94.1	MRID 00106830
oats, straw	MRID 00106830	M-539.1	0.05-1.0	73.1-116.5	MRID 00106830
peanut foliage	MRID 00051961	M-580	0.05-1.0	74.1-107.5	MRID 00051958
peanut hay	MRID 00051961	M-580	0.05-1.0	97.0-123.1	MRID 00051958
peanut hulls	MRID 00051961	M-580	0.05-1.0	71.0- 97.8	MRID 00051958
peas	MRID 00070962	M-742	0.05-5.0	74-114	MRID 00070962
pea vines	MRID 00070962	M-742	0.05-5.0	67-124	MRID 00070962
potato tubers	MRID 00039528	M-615	0.05-1.0	68.0-125.9	MRID 00039526
potato vines	MRID 00039529	M-616	0.05-1.0	99.0-137.2	MRID 00039526
sorghum forage	MRID 00106791	M-745	0.05-5.0	63.0-129.0	MRID 00106791
sorghum fodder	MRID 00106791	M-745	0.05-5.0	88.0-134.0	MRID 00106791
soybean foliage	MRID 00106830	M-531	0.05-1.0	79.6-105.8	MRID 00041898
soybean green seed	MRID 00041904	M-561	0.05-1.0	70.6-101.3	MRID 00041898
sunflower straw	PP#0F2372(242640)	M-706	0.05-5.0	92-120	PP#0F2372(242640)
wheat foliage	MRID 00106808	M-522.1	0.05-1.0	71.4-120.7	MRID 00106830
wheat straw	MRID 00106808	M-522.1	0.05-1.0	66.2-116.9	MRID 00106830

STORAGE STABILITY DATA

Conclusions:

The storage stability of pendimethalin residues in or on animal and plant samples is not adequately understood. The following additional data are required:

- Data reflecting the stability of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite (CL 202,347) in or on representative plant [such as root and tuber vegetables, legume vegetables, cereal grains, and miscellaneous crops (cottonseed, peanuts, and sunflower seed)] and animal samples stored at freezing temperatures for time intervals approximating those of the treated samples used to determine the magnitude of the residue.

References (used):

American Cyanamid Co. 1980. PROWL* pendimethalin (CL 92,553): Validation of GC method M-1113 for the determination of CL 99,900 residues in water. Report No. C-1791 by A.J. Manuel submitted under PP#0F2401(099889).

Discussion of the data:

American Cyanamid Co. submitted a study (Report No. C-1791 in PP#0F2401) in which water was fortified with the 4-carboxylic acid metabolite (CL 99,900) of pendimethalin at 1 and 5 ppb and stored under freezing conditions for 1 and 2 months. In two samples fortified at 1 ppb, 110.0 and 112.7% of the initial concentration was recovered after 1 and 2 months, respectively, and in two samples fortified at 5 ppb, 99.8 and 97.7% of the initial concentration was recovered after 1 and 2 months, respectively.

The above data do not reflect the stability of pendimethalin residues in or on agricultural commodities and has been presented for general information purposes only. We believe the available data to be inadequate because no agricultural commodities were tested.

MAGNITUDE OF THE RESIDUE IN PLANTS

Additional metabolism studies are required. If new metabolites of residue concern are found, then additional field residue studies for all r.a.cs may be needed. Additional field residue studies may also have to include any manufacturing impurities if they are found to be present in the technical material at a level of Toxicological concern.

Root and Tuber Vegetables Group

Conclusions for the Root and Tuber Vegetables Group:

A crop group tolerance is not appropriate at the present time for the following reasons:

- Residue data are required for three additional representative members of this crop group (carrot, radish, and sugar beet).

- Additional residue data are required to support the established tolerance for pendimethalin residues in or on potatoes (refer to the following section for details of data gaps).

Potatoes

Tolerance:

A tolerance of 0.1 ppm has been established for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on potatoes (40 CFR 180.361).

Use directions and limitations:

The 4 lb/gal EC formulation has been registered for use for potatoes at 0.50-1.5 lb ai/A as a preemergence or preemergence incorporated (into the top 1-2 inches of soil) broadcast or band application. A single treatment is made after planting or before, at, or after drag-off but before weeds and potatoes emerge (incorporation is performed 7 days after treatment prior to planting or before, at, or after drag-off). Aerial and ground equipment may be used. Irrigation sprinkler systems may also be used for application in all states excluding CA. This formulation may be tank mixed with eptam or metribuzin. For application in irrigation water, 0.5-0.75 inches is to be used. A 24(c)

registration has been issued for ME (EPA Reg. No. ME-810001) for use of the 4 lb/gal EC at a maximum rate of 1.5 lb ai/A as a preemergence application (not to be incorporated) using ground equipment. A treatment is to be made once after planting before weeds and potatoes emerge and is to be tank mixed with linuron.

Conclusions:

Sufficient data are available to fully support the established tolerance for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on potatoes.

Due to the fact that no detectable residues (<0.05 for each compound) are indicated to result from exaggerated uses (2.67x) we are of the opinion that no detectable residues will result in dried potatoes, granules and potato chips.

No Canadian or Mexican tolerances or Codex MRL exist for pendimethalin residues in or on potatoes.

Reference (used):

American Cyanamid Co. 1978. Amounts of residues of PROWL, its metabolite (CL 202,347) metribuzin (sencor or lexone) and eptam in or on potatoes. Report Nos. C-787, C-789, C-790, C-1013, C-1014, C-1015, C-1016, C-1017, C-1087, C-1088, C-1089, C-1090, C-1091, C-1094, C-1095, C-1096, C-1183, C-1378, C-1379, C-1380, C-1381, C-1382, C-1383, C-1384, C-1385, C-1386, C-1387, C-1388, C-1389, C-1390, C-1391, C-1392, C-1393, C-1394, and C-1395. Compilation; unpublished study submitted under EPA Reg. No. 241-243. (CDL Nos. 097433-A and 097434; MRID No. 00106797).

Discussion of the data:

American Cyanamid Co. (MRID No. 00106797) submitted residue data involving pendimethalin residues in or on potatoes from tests conducted in AZ (3), CA (2), CO (6), FL (6), ID (4), MD (2), ME (13), MN (2), MT (5), ND (3), NJ (2), NY (5), PA (2), OR (6), WA (4), and WI (17); the number of tests per state is parenthesized. The combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite (CL 202,347) were nondetectable at <0.10 ppm (includes pendimethalin at <0.05 ppm and its metabolite at <0.05 ppm) in all of the data submitted which involved 111 samples of potatoes and four samples of potato vines. Treatment regimes involved a preemergence application (with or without incorporation; before, at, or after drag-off) of the 4 lb/gal EC formulation at 0.75-4 lb ai/A (0.5-2.67x the maximum use rate; represents 91 samples of potato tubers [43 of these involved a tank mix with either eptam or metribuzin] and four samples of vines) using sampling intervals of 69-162 days, or a postemergence application (not a registered use) of the same formulation at 0.75 lb ai/A (0.5x; represents six tuber samples) using sampling intervals of 60 and 90 days. A preplant-incorporated application was made using the 4 lb/gal EC at 0.75 lb ai/A (0.5x; one tuber sample). The 3 lb/gal EC formulation (currently not registered for use on potatoes) was also used as a test substance; a preemergence application at 1-3 lb ai/A (0.67-2x; 13 tuber samples) was made using sampling intervals of 114-143 days. All applications of pendimethalin formulations were made using ground equipment.

Adequate analytical methods (Method No. M-613, M-615, and M-616; GC with electron capture detection) were used for data collection. The states of AZ (<1%), CA (6.2%), CO (4.2%), FL (2%), ID (24%), MD (<1%), ME (8%), MN (4.4%), MT (<1%), ND (6%), NJ (<1%), NY (4%), PA (1.6%), OR (6.5%), WA (15.7%), and WI (5.4%) that were used as test sites provide adequate geographic representation because together they contribute approximately 88% to the total U.S. potato crop (Agricultural Statistics, 1982, p. 167); the percentage of each state's contribution is parenthesized.

Residue data were not submitted involving application of pendimethalin using aerial equipment; however, we feel submission of such data is not necessary because treatment is made preemergence and adequate data were provided for preemergence treatment using ground equipment in which no detectable residues (<0.10 ppm) were found in or on potatoes even at exaggerated rates (2.67x). For the same reason, we believe that data, which were not provided, involving preemergence application of pendimethalin by irrigation sprinkler are also not required. We conclude that the combined residue of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on potatoes are not expected to exceed the established 0.1 ppm tolerance following the registered method of use and maximum application rate.

Since no detectable residues (<0.05 ppm) resulted from the maximum registered uses and even from exaggerated rates (2.67x) in or on potatoes we are of the opinion that no detectable residues will result in processed commodities i.e. dried potatoes, potato chips and granules and that no additional data are required.

Legume Vegetables Group

Conclusions for the Legume Vegetables Group:

A crop group tolerance is not appropriate at the present time for the following reason:

- Pendimethalin formulations are currently registered for use only on soybeans; data are required for two additional members of this group [beans (one succulent variety and one dried variety), and peas (one succulent variety and one dried variety)]. Data for beans (dried, lima, and snap) and peas (dried and succulent) in support of proposed tolerances for these commodities are currently under review.

Beans (dry, lima, and snap)

Tolerances:

Tolerances have not been established for residues of pendimethalin in or on dry beans, lima beans, or snap beans because the data in support of these proposed tolerances are currently under review. Tolerances of 0.1 ppm for residues of pendimethalin per se and its metabolite (CL 202,347) have been proposed for dry beans, lima beans, and snap beans (1981, PP#1F2567).

Use directions and limitations:

The 4 lb/gal EC formulation is proposed for use on beans (dry, lima, and snap) at 0.5-1.5 lb ai/A depending on soil characteristics. A single preplant application (broadcast on band) may be made alone or in a tank-mix with S-ethyl dipropylthiocarbamate (EPTC). This proposed use pattern was obtained from an EPA memorandum by A. Smith, dated April 29, 1982 (in correspondence file for PP#1F2567).

Conclusions:

The available data in support of the proposed tolerances for residues of pendimethalin per se and its metabolite (CL 202,347) are currently under review. There are no Mexican or Canadian tolerances, nor are there Codex MRLs for pendimethalin residues in or on dry beans, lima beans, or snap beans.

References:

N/A.

Discussion of the data:

N/A.

Peas (dried and succulent)

Tolerances:

Tolerances have not been established for residues of pendimethalin in or on shelled peas, pea pods, or peas plus pods because the data in support of these proposed tolerances are currently under review. Tolerances of 0.1 ppm for residues of pendimethalin per se and its metabolite (CL 202,347) have been proposed for shelled peas, pea pods, and peas plus pods (1983, PP#3F2792). Note that the correct commodity expression for peas is "peas (dried and succulent)". EPA has recommended that the petitioner submit a revised Section F proposing the tolerances as stated above (EPA memorandum by R. Perfetti, dated September 23, 1983; in correspondence file of PP#3F2792).

Use directions and limitations:

The 4 lb/gal EC formulation is proposed for use on peas at 1.5 lb ai/A. Broadcast or band applications are to be made preplant once per crop season using ground or aerial equipment; soil incorporation should follow soon after

treatment. This proposed use pattern was obtained from an EPA memorandum by R. Perfetti, dated March 9, 1983 (in correspondence file for PP#3F2792).

Conclusions:

The available data in support of the proposed tolerances for residues of pendimethalin per se and its metabolite (CL 202,347) are currently under review. There is no Canadian or Mexican tolerance, nor is there a Codex MRL for pendimethalin residues in or on peas (dried or succulent).

References:

N/A.

Discussion of the data:

N/A.

Soybeans

Tolerance:

A tolerance of 0.1 ppm has been established for the combined residues of pendimethalin and its metabolite 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol (CL 202,347) in or on soybeans (40 CFR 180.361).

Use directions and limitations:

The 4 lb/gal EC and the 60% dispersible granule (DG) formulations are registered for use on soybeans (except in CA) at 0.5-2 lb ai/A. A single, preplant broadcast or band application (aerially or ground-applied) is incorporated within 7 days of application. The 4 lb/gal EC and 60% DG formulations are also registered for preemergence (at-planting or 2 days after planting for no-till soybeans) applications at 0.5-1.25 lb ai/A. The formulations may be applied using aerial or ground equipment and may be tank-mixed with other herbicides.

Conclusions:

The available data partially support the established tolerance for pendimethalin residues in or on soybeans and are sufficient to determine that the label directions are adequate. However, because insufficient processing data were submitted the concentration of pendimethalin residues in processed commodities is not adequately detailed.

A review of the raw data for the seed crops indicates that the reported "non-detectable" residue level (<0.05 ppm) for pendimethalin and its metabolite CL 202.347 may account for apparent combined residues not to exceed 0.016 ppm in corn, 0.011 ppm in cottonseed, 0.010 ppm in soybeans, 0.011 ppm in peanuts and 0.012 ppm in sunflower as a result from the maximum registered use. Due to the fact that residues in seed crops may concentrate during processing to oil to the extend of 6x for soybeans and as much as 25x for corn, there is a concern that combined residues of pendimethalin and CL 202.347 in processed oil may exceed the established tolerance of 0.1 ppm for the individual raw agricultural commodity. Since additional metabolism studies are requested, the request for an additional processing study for soybeans will depend upon the results of the final residues of concern. If requested, this processing study will be translated to cottonseed, peanuts, corn, sunflower seed, and may also be translated to support the pending safflower seed tolerance.

No Codex MRL or Canadian or Mexican tolerance exists for pendimethalin residues in or on soybeans.

References (used):

Boughton, P.J., Moyer, M., Kust, C.A., et al. 1974. PROWL® (CL 92,553): Determination of CL 92,553 [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] and CL 202,347 [4-([1-ethylpropyl]amino)-2-methyl-3,5-dinitrobenzyl alcohol] residues in soybean seeds. Unpublished study including Report Nos. C-542, C-545, C-546, C-547, C-549, C-551, C-552, C-553, C-580, C-582, C-584 and C-585 received Dec. 21, 1974 under PP#5G1580; submitted by American Cyanamid Co. (CDL:094331-K; MRID:00029801).

American Cyanamid Co. 1975. General summary--PROWL herbicide residues in soybean plants, seeds, oil, meal and soil. [Includes summary of Report Nos. C-768, C-551.1, C-552.1, C-769, and C-545.1]. Unpublished study received Nov. 20, 1975 under PP#6F1704. (CDL:094648-A; MRID:00041897).

Boughton, P.J., Moyer, M., Kust, C.A., et al. 1976. Residues of PROWL herbicide and its metabolite in cotton and soybeans. [Includes Report Nos. C-543, C-543.1, C-544, C-548, C-548.1, C-550, C-550.1, C-579, C-581, C-583, and C-583.1]. Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-A; MRID:00025818).

Discussion of the data:

American Cyanamid Co. (MRIDs 00025818, 00029801, and 00041897) submitted data pertaining to the combined residues of pendimethalin per se and its metabolite (CL 202,347) in or on soybean seed (green and dry) from tests conducted in AL (1), GA (1), IA (6), IL (4), IN (3), KS (8), LA (3), MN (3), MO (5), MS (2), NC (4), OH (4), OK (2), and TN (2); the number of tests per state is given in parentheses. Combined residues were nondetectable [<0.1 ppm, including pendimethalin per se at <0.05 ppm (ND) and CL 202,347 at <0.05 ppm (ND)] in or on nine green soybean seed samples collected 102-165 days following a single preemergence or preplant incorporated application of the 3 or 4 lb/gal EC formulation at 0.75-2 lb ai/A (0.38x-1x the maximum registered rate) alone or in combination with metribuzin in a tank-mix or as a sequential application. All applications were made using ground equipment. Dry soybean seed (40 samples) harvested 108-220 days after an identical treatment also yielded nondetectable combined residues (<0.01 ppm).

American Cyanamid Co. (MRID 00025818) also submitted processing studies (Report Nos. C-550.1 and C-583.1) in which two soybean seed samples bearing nondetectable (<0.1 ppm, including pendimethalin per se at <0.05 ppm and CL 202,347 at <0.05 ppm) residues were processed into oil and meal; residues in oil and meal were also nondetectable (<0.05 ppm for pendimethalin and <0.05 ppm for CL 202,347). This processing study is inadequate for the following reasons: (i) hulls and soapstock were not analyzed; and (ii) residues were nondetectable in the seed used for processing (therefore, concentration factors cannot be determined). We feel that an additional study is required because solvent extraction of oil from seed crops is expected to remove virtually all residues of concern from oil seeds. This is based on the fact that hexane extraction efficiently removes both pendimethalin and CL 202,347

from oil seeds (refer to Tables 2 and 3 in the Residue Analytical Methods section). Therefore, even nondetectable residues in seed may concentrate in oil to levels which exceed the established tolerance for residues in or on the seed.

Adequate electron capture GC methods were used for residue quantitation for the following commodities: green soybean seed (M-560 and M-561), dry soybean seed (M-533 and M-536), soybean oil (M-602 and M-603), and soybean meal (M-604 and M-605). Adequate geographic representation is provided by AL, GA, IA, IL, IN, KS, LA, MN, MO, MS, NC, OH, and TN since these states produced 78% of the total 1981 U.S. soybean crop (Agricultural Statistics, 1982, p. 131). In our opinion, the available data partially support the established tolerance (0.1 ppm) for pendimethalin residues in or on soybeans. A processing study may be required for soybeans. For particulars see Conclusions of this topic.

Foliage of Legume Vegetables Group

Conclusions for the Foliage of Legume Vegetables Group:

A crop group tolerance is not appropriate at the present time for the following reasons:

- Additional data are required to support the established tolerance for soybean hay (refer to Soybean forage and hay section for details of data gaps).

- The data do not support the soybean forage tolerance (refer to Soybean forage and hay section for a possible solution to this problem).

- Pendimethalin formulations are currently registered for use only on soybeans; data are required for two additional members of this group (beans and field peas). Data for bean foliage and straw and pea vines in support of proposed tolerances for these commodities are currently under review.

Bean forage and hay

Tolerances:

Tolerances have not been established for residues of pendimethalin in or on bean foliage and straw because the data in support of these proposed tolerances are currently under review. Tolerances of 0.1 ppm have been proposed for residues of pendimethalin per se and its metabolite (CL 202,347) in or on bean foliage and straw (1981, PP#1F2567). Note that a more appropriate expression for the bean foliage and straw tolerances is bean forage and bean hay, respectively.

Use directions and limitations:

The 4 lb/gal EC formulation is proposed for use on beans (dry, lima, and snap) at 0.5-1.5 lb ai/A, depending on soil characteristics. A single, pre-plant application (broadcast or band) may be made alone or in a tank-mix with S-ethyl dipropylthiocarbamate. Livestock may not forage or graze or be fed bean hay or vines from bean fields treated with tank mixes of pendimethalin and S-ethyl dipropylthiocarbamate. This proposed use pattern was obtained from an EPA memorandum by A. Smith, dated April 29, 1982 (in correspondence file for PP#1F2567).

Conclusions:

The available data in support of the proposed tolerances for residues of pendimethalin *per se* and its metabolite (CL 202,347) are currently under review. There is no Canadian or Mexican tolerance, nor is there a Codex MRL for pendimethalin residues in or on bean forage and hay.

References:

N/A.

Discussion of the data:

N/A.

Pea Vines

Tolerance:

A tolerance has not been established for pendimethalin residues in or on pea vines because the data in support of this proposed tolerance are currently under review. A tolerance of 0.1 ppm for residues of pendimethalin *per se* and its metabolite (CL 202,347) has been proposed for pea vines (1983, PP#3F2792).

Use directions and limitations:

The 4 lb/gal EC formulation is proposed for use on peas at 1.5 lb ai/A. Broadcast or band applications are to be made preplant once per crop season using ground or aerial equipment; soil incorporation should follow soon after treatment. This proposed use pattern was obtained from an EPA memorandum by R. Perfetti, dated March 9, 1983 (in correspondence file for PP#3F2792).

Conclusions:

The available data in support of the proposed tolerance for residues of pendimethalin per se and its metabolite (CL 202,347) are currently under review. There is no Canadian or Mexican tolerance, nor is there a Codex MRL for pendimethalin residues in or on pea vines.

References:

N/A.

Discussion of the data:

N/A.

Soybean forage and hay

Tolerances:

Tolerances of 0.1 ppm have been established for the combined residues of pendimethalin and its metabolite (CL 202,347) in or on soybean forage and hay (40 CFR 180.361).

Use directions and limitations:

The 4 lb/gal EC and the 60% dispersible granule (DG) formulations are registered for use on soybeans (excluding CA) at 0.5-2 lb ai/A. A single, preplant broadcast or band application (aerially or ground-applied) is incorporated within 7 days of application. The 4 lb/gal EC and 60% DG formulations are also registered for preemergence application to no-till soybeans (at-planting or 2 days after planting) at 0.5-1.25 lb ai/A. The formulations may be applied using aerial or ground equipment and may be tank-mixed with other herbicides.

Conclusions:

The available data do not support the established tolerance for pendimethalin residues in or on soybean forage because several residue values were tolerance-exceeding. The data indicate that a 60-day pregrazing and prefeeding restriction should be proposed. In addition, a soybean straw tolerance must be proposed. Also, no data are available to support the established tolerance for soybean hay. The following data are required:

- Data reflecting combined residues of pendimethalin *per se* and CL 202,347 in or soybean hay and straw harvested 60 days after an at-planting application (made with aerial or ground equipment) of the 4 lb/gal EC or 60% DG formulation at 2 lb ai/A. Tests must be conducted in IL, MN, and MO; these states represent the major U.S. soybean production areas (Agricultural Statistics, 1982, p. 131).

There is no Canadian or Mexican tolerance or Codex MRL for residues of pendimethalin in or on soybean forage, hay or straw.

References (used):

Boughton, P.J., Moyer, M., Kust, C.A., et al. 1974. PROWL® (CL 92,553): Determination of CL 92,553 [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] and CL 202,347 [4-([1-ethylpropyl]amino)-2-methyl-3,5-dinitrobenzyl alcohol] residues in soybean seeds. Unpublished study including Report Nos. C-542, C-549, C-580, C-582, C-584, and C-585 received Dec. 21, 1974 under PP#5G1580; submitted by American Cyanamid Co. (CDL:094331-K; MRID:00029801).

Boughton, P.J., Moyer, M., Kust, C.A., et al. 1976. Residues of PROWL herbicide and its metabolite in cotton and soybeans. [Includes Report Nos. C-548, C-583, C-581, C-579, and C-550.] Unpublished study received Feb. 13, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:241781-A; MRID:00025818).

Discussion of the data:

American Cyanamid Co. (MRIDs 00025818 and 00029801) submitted data pertaining to the combined residues of pendimethalin per se and its metabolite (CL 202,347) in or on soybean foliage from the following test locations (the number of tests/states follows in parentheses): AR (1), IA (4), IL (2), IN (1), KS (4), MN (2), MO (2), MS (1), OH (2), and OK (1). All samples received a single, ground-applied preemergence or preplant incorporated application of the 3 or 4 lb/gal EC formulation at 1-2 lb ai/A (0.5x-1x the maximum registered rate). Combined residues were nondetectable [<0.01 ppm, including pendimethalin per se at <0.05 ppm and CL 202,347 at <0.05 ppm] in or on 23 soybean foliage samples harvested 76-165 days posttreatment; at shorter harvest intervals of 27-62 days, 10 additional samples also yielded nondetectable combined residues. However, two OH samples (Report C-583) and one IL sample (Report C-582), also collected 27-63 days following identical treatment, bore combined residues of <0.1 ppm (including nondetectable levels of pendimethalin and CL 202,347 each at <0.05 ppm each) to <0.123 ppm [including pendimethalin per se at 0.073 ppm and CL 202,347 at <0.05 ppm (ND)]; these data represent six determinations on three samples. No data were submitted pertaining to residues of pendimethalin in or on soybean hay or straw.

Adequate electron capture GC methods (M-483.1 and M-531) were used for residue quantification. Adequate geographic representation is provided by IA, IL, IN, KS, MN, MO, MS, and OH since these states collectively contributed 66% of the total 1981 U.S. soybean production (Agricultural Statistics, 1982, p. 131). The available data do not support the established tolerances for pendimethalin residues in or on soybean forage; a 60-day pregrazing and prefeeding interval should be proposed. Additionally, no data were submitted for soybean hay or straw; accordingly, we have required additional data for these commodities. We conclude that the tolerances for soybean forage and hay are not adequately supported. Also, a tolerance for pendimethalin residues in or on soybean straw must be proposed.

Fruiting Vegetables (Except Cucurbits) Group

Conclusions for the Fruiting Vegetables (Except Cucurbits) Group:

A crop group tolerance is not appropriate at the present time for the following reason:

- Residue data are required for the two representative members (tomatoes and peppers) of this crop group. Currently no tolerance exists for any member of this group; however, a tolerance for pendimethalin residues in or on tomatoes is pending.

Tomatoes

Tolerance:

A tolerance does not exist at present for pendimethalin residues in or on tomatoes. A tolerance of 0.1 ppm for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite has been proposed by American Cyanamid Co. (1984, PP#4F3042) and is currently pending.

Use directions and limitations:

The 4 lb/gal EC formulation has been proposed for use on tomatoes in southern states (including eastern coastal plains) in coarse textured soils at 0.5-0.75 lb ai/A, in medium textured soils at 0.75-1 lb ai/A, and in fine textured soils at 0.75-1.5 lb ai/A. In northern states, the 4 lb/gal EC is proposed for use at 0.5-1 lb ai/A in coarse soils containing ≤3% organic matter (at 1 lb ai/A for >3% organic matter), at 0.75-1.25 lb ai/A in medium soils containing ≤3% organic matter (at 1.25-1.5 lb ai/A for >3% organic matter), and at 1-1.5 lb ai/A in fine soils containing ≤3% organic matter (at 1.5 lb ai/A for >3% organic matter). Treatment of direct-seeded tomatoes is proposed as a postemergence incorporated application (direct spray to soil - not to be applied over tomato foliage) at blocking or thinning using ground equipment

and treatment of transplanted tomatoes is proposed as a preplant incorporated application using ground or aerial equipment. The formulation is not to be used on peat or muck soils.

Conclusions:

Available data in support of the proposed tolerance for pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on tomatoes are currently under review. Therefore, the adequacy of the data cannot be assessed at the present time. No Canadian or Mexican tolerance or Codex MRL exists for pendimethalin residues in or on tomatoes.

References:

N/A.

Discussion of the data:

N/A.

Cereal Grains Group

Conclusions for the Cereal Grains Group:

A crop group tolerance is not appropriate at the present time for the following reason:

- Proposed tolerances for three representative members (barley, sweet corn, and wheat) of this crop group are currently pending; tolerances have been established for three other representative members (field corn, rice, and sorghum). When and if the currently pending tolerances are established, a crop group tolerance should be considered at that time.

Barley grain

Tolerance:

A tolerance of 0.1 ppm for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite (CL 202,347) in or on barley grain has been proposed by American Cyanamid Co. (1983, PP# 3F2788) and is currently pending.

Use directions and limitations:

The 4 lb/gal EC formulation has been proposed for use on barley at 1.5 lb ai/A as a preemergence treatment made using either ground or aerial equipment (EPA memorandum from R. Perfetti [RCB/HED] to R. Taylor [FHB,RD] and Toxicology Branch in correspondence file of PP# 3F2788; dated March 9, 1983).

Conclusions:

Available data in support of the proposed tolerance for pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on barley grain are currently under review. Therefore, the adequacy of the data cannot be assessed at the present time. No Canadian or Mexican tolerances or Codex MRL exist for pendimethalin residues in or on barley grain.

References:

N/A.

Discussion of the data:

N/A.

Corn grain

Tolerance:

A tolerance has been established for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite (CL 202,347) in or on field corn grain at 0.1 ppm (40 CFR 180.361).

Use directions and limitations:

The 10% G, 3 lb/gal EC, 4 lb/gal EC, and 60% DG (dispersible granules) formulations have been registered for use on field corn at 0.75-2 lb ai/A as a preemergence application (broadcast or band) made after planting before weeds and crop emerge using ground equipment; the 4 lb/gal EC and 60% DG may be applied using aerial equipment. The 10% G and 3 lb/gal EC formulations are not to be used on sands or loamy sands or on soils containing <1.5% organic matter.

The 4 lb/gal EC has been registered for an early postemergence application (broadcast or band) at 1-1.5 lb ai/A (tank mixed with atrazine or cyanazine WP formulations) using ground or aerial equipment; application is to be made no later than the 2-leaf growth stage and when weeds are ≤1 inch tall and may not follow a preemergent pendimethalin application. This same formulation may be used as a postemergence incorporated treatment at 0.5-1.5 lb ai/A using ground equipment from the 4-inch growth stage up to the last cultivation. Several uses involve tank mixes with other herbicides. Treated forage may not be fed to, or grazed by, livestock until 21 days after treatment.

The states of CO (EPA SLN No. CO-790014), KS (EPA SLN No. KS-790009), NE (EPA SLN No. NE-790007), and TX (EPA SLN No. TX-780018) have been issued state label registrations under Section 24(c) for use of the 4 lb/gal EC formulation on field corn at 0.75-1.5 lb ai/A as a postemergence incorporated application used alone or tank mixed with atrazine and applied with ground equipment.

Conclusions:

Sufficient data are not available to assess the adequacy of the established tolerance and label directions because insufficient processing data were submitted.

A review of the raw data for the seed crops indicates that the reported "non-detectable" residue level (<0.05 ppm) for pendimethalin and its metabolite CL 202.347 may account for apparent combined residues not to exceed 0.016 ppm in corn, 0.011 ppm in cottonseed, 0.010 ppm in soybeans, 0.011 ppm in peanuts and 0.012 ppm in sunflower as a result from the maximum registered use. Due to the fact that residues in seed crops may concentrate during processing to oil to the extend of 6x for soybeans and as much as 25x for corn, there is a concern that combined residues of pendimethalin and CL 202.347 in processed oil may exceed the established tolerance of 0.1 ppm for the individual raw agricultural commodity. Since additional metabolism studies are requested, the request for an additional processing study for soybeans will depend upon the results of the final residues of concern. If requested, this processing study will be translated to cottonseed, peanuts, corn, sunflower seed, and may also be translated to support the pending safflower seed tolerance.

No Canadian or Mexican tolerance or Codex MRL exist for pendimethalin residues in or on field corn.

References (used):

American Cyanamid Co. 1981. Residues of Prowl. Report Nos. C-1327, C-1328, C-1495, C-1496, C-1497, C-1498, C-1499, C-1891, C-1895, and C-1896. Compilation; unpublished study, including published data, submitted under EPA Reg. No. 241-243. (CDL:246583-A; MRID:00093697).

American Cyanamid Co. 1978 Amounts of residues of Prowl, its metabolite (CL 202,347), Atrazine, and Bladex in or on field corn. Report Nos. C-874, C-899, C-900, C-903, C-1064, C-1336, C-1337, C-1341, C-1342, and C-1343. Compilation; unpublished study submitted under EPA Reg. No. 241-243. (CDL:-233898-A; MRID:00106820).

Bodnarchuk, D., Laporta, M., Potts, C., et al. 1975. Summary--PROWL and Banvel-- residues in corn plants. Report Nos. C-875 and C-876. Unpublished study submitted by American Cyanamid Co. under EPA Reg. No. 241-243. (CDL:-230428-A; MRID:00030693).

Bodnarchuk, Wyckoff, J.C., Nzewi, G.I. 1974. Prowl (CL 92,553): Determination of CL 92,553...and CL 202,347...residues in field corn tissues: Report No. C-450. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474-M; MRID:00023788).

Moyer, M., Potts, C., Bodnarchuk, D., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., and Atrazine...and Bladex... residues in field corn tissues: Report No. C-461. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474-P; MRID:0002-3791).

Moyer, M., Potts, C., Wyckoff, J.C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...residues in field corn tissues: Report No. C-463. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474-Q; MRID:00023792).

Moyer, M., Potts, C., Wyckoff, J.C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-464. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474-R; MRID:00023793).

Wyckoff, J.C., Bodnarchuk, D., Moyer, M., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in corn tissues: Report No. C-456. Unpublished study received under PP#-5F1556; submitted by American Cyanamid Co. (CDL:094474-N; MRID:00023789).

Wyckoff, J.C., Bodnarchuk, D., Moyer, M., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553...and CL 202,347...residues in field corn tissues: Report No. C-459. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474-L; MRID:00023787).

Wyckoff, J.C., Bodnarchuk, D., Moyer, M., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-466. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474; MRID:00023795).

Wyckoff, J.C., Moyer, M., Bodnarchuk, D., et al. 1973. Prowl (CL 92,553): Determination of CL 92,553...CL 202,347...Atrazine...and Bladex...residues in field corn tissues (fodder and grain): Report No. C-401. Unpublished study received under PP#4G1451; submitted by American Cyanamid Co. (CDL:093869-0; MRID:00029029).

Wyckoff, J.C., Bodnarchuk, D., Nzewi, G.I. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-460. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474-0; MRID:00023790).

Wyckoff, J.C., Bodnarchuk, D., Potts, C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553...and CL 202,347...residue in field corn tissues (grain and forage): Report No. C-457. Unpublished study received under PP#-5F1556; submitted by American Cyanamid Co. (CDL:094474-K; MRID:00023786).

Wyckoff, J.C., Moyer, M., Potts, C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-465. Unpublished study received under PP#5F1556; submitted by American Cyanamid Co. (CDL:094474-S; MRID:00023794).

Discussion of the data:

Residue data were submitted by American Cyanamid Co. (MRID Nos. 00093697, 00-106820, 00023786, 00023790, 00023789, 00029029, 00023788, 00023787, 00023793, 00023791, 00023795, 00023794, 00023792, and 00030693) involving pendimethalin residues in or on field corn grain from 83 tests conducted in CA (1), CO (10), IA (6), IL (12), IN (1), KS (2), KY (2), MO (1), MN (5), NE (11), NY (11), OH (5), SD (6), TX (6), and WI (4); the number of tests per state is parenthesized. The combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol

metabolite were nondetectable at <0.1 ppm (includes pendimethalin and its metabolite at <0.05 ppm each) in or on 111 samples of field corn grain and four samples of popcorn grain (no tolerance exists for pendimethalin residues in or on popcorn grain). Treatment regimes included the use of the 4 lb/gal EC formulation at 0.75-2 lb ai/A (0.38x-1x the maximum registered use rate) as a preemergence or postemergence application with or without incorporation. Pendimethalin was applied either alone (involved 56 samples) or tank-mixed with either atrazine (18 samples), cyanazine (six samples), or dicamba (three samples) using ground equipment and sampling intervals of 85-172 days. Thirteen of the grain samples were from plots treated preemergence or preplant prior to the pendimethalin application with either atrazine, Eradicane, Sutan, or atrazine and alachlor. Using aerial equipment, this same formulation was applied postemergence (plants were 8-10 inches tall) and incorporated at 1 lb ai/A (0.5x), and after 108 days, two samples of grain contained nondetectable (<0.1 ppm) residue levels. To generate some samples, the 3 lb/gal EC formulation was used in a preemergence application at 1.5-6 lb ai/A (0.75x-3x) using ground equipment and sampling intervals of 125-179 days applied alone (involved 18 samples) or tank-mixed with either atrazine (seven samples) or cyanazine (seven samples). The available data did not involve the use of the 10% G or 60% DG formulations (also registered for use on field corn) as test substances; however, because all residue values were nondetectable in or on 111 samples of grain as the result of the application of 4 lb/gal EC or 3 lb/-gal EC, we feel additional field corn grain data are not necessary. However, we do believe that an oilseed processing study may be required because sub-tolerance residue levels (<0.1 ppm) in corn grain may concentrate during processing to oils and possibly exceed the established tolerance for grain. We would not expect residues to concentrate in milled products from corn grain.

Data from the additional processing study requested for soybeans will be translated to corn. For particulars see p. 61.

Adequate analytical GC methods (Method Nos. M-465 and M-466) employing electron capture detection were used for data collection. Geographic representation was adequate because the states of CA (<1%), CO (1%), IA (26%), IL (13%), IN (8%), KS (2%), KY (2%), MO (3%), MN (9%), NE (10%), NY (<1%), OH (4%), SD

(2%), TX (1%), and WI (5%) represent a combined 91-93% of the total U.S. production of corn grain (Agricultural Statistics, 1982, p. 32); the percent contribution to the total production by each individual state is parenthesized. We conclude that the available data involving field corn grain are adequate and that pendimethalin residues in or on field corn grain are not expected to exceed the established tolerance following the registered method of use. However, data are needed involving pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on the processed products (crude and refined oil) of field corn grain.

Corn, sweet

Tolerance:

A tolerance has been proposed by American Cyanamid Co. (1982, PP#2F2628) for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sweet corn grain at 0.1 ppm and is currently pending.

Use directions and limitations:

The 4 lb/gal EC formulation has been proposed for use on sweet corn (processing varieties only) at 0.75-2 lb ai/A as a preemergence or postemergence (no later than the 2-leaf growth stage) treatment used alone or tank mixed with atrazine or cyanazine in MN and WI only; air or ground equipment may be used [EPA memorandum from A. Smith (RCB) to R. Taylor (Registration Division) in correspondence file of PP#2F2628].

Conclusions:

Available data in support of the proposed tolerance for pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sweet corn grain are currently under review. Therefore, the adequacy of the data cannot be assessed at the present time. No Canadian or Mexican tolerances or Codex MRL exist for pendimethalin residues in or on sweet corn grain.

References:

N/A.

Discussion of the data:

N/A.

Rice grain

Tolerance:

A tolerance of 0.05 ppm has been established for residues of pendimethalin *per se* and its metabolite (CL 202,347) in or on rice grain (40 CFR 180.361).

Use directions and limitations:

The 4 lb/gal EC formulation is registered for use on dry-seeded rice at 0.75-1 lb ai/A. A single, annual postemergence application may be made with ground or aerial equipment. Irrigation by rainfall or irrigation flush should be received within 7 days of application; no flood water should be on fields at the time of application. Use on rice grown in CA is not permitted. Rice straw from treated fields may not be baled for use as feed or bedding. Use on water-seeded rice is not permitted.

Conclusions:

The available data do not fully support the established tolerance of 0.05 ppm for the combined residues of pendimethalin and its CL 202,347 metabolite in or on rice grain because the limit of detection for these combined residues is 0.1 ppm. We therefore recommend that the tolerance be increased to 0.1 ppm. No additional data are required for residues of CL 202,347 in or on rice grain because the rice metabolism study [refer to Nature of the Residue in Plants; Marei, *et al.* (1974)] and studies utilizing other grains provide supportive data which indicate that combined residues of pendimethalin *per se*

and its CL 202,347 metabolite in or on rice grain will not exceed 0.1 ppm. There is no Canadian or Mexican tolerance, nor is there a Codex MRL, for residues of pendimethalin in or on rice grain.

References (used):

American Cyanamid Co. 1980. Residues of Prowl herbicide. Compilation [includes Report Nos. C-1793, C-1796, C-1797, and C-1799]; unpublished study received Jan. 22, 1981 under 241-243. (CDL:099888-C; MRID:00071120).

American Cyanamid Co. 1980. Summary of residue analysis for Prowl herbicide in rice grain. Compilation [includes Report Nos. C-1674, C-1687, C-1695 to C-1697, and C-1702]; unpublished study received Aug. 25, 1980 under 241-243. (CDL:099565-A; MRID:00067283).

Discussion of the data:

American Cyanamid Co. (MRIDs 00067283 and 00071120) submitted data pertaining to residues of pendimethalin *per se* in or on rice grain and straw from tests (the number of tests per state is given parenthetically) conducted in AR (8), LA (3), MS (1), and TX (6). Pendimethalin residues were nondetectable (<0.05 ppm) in or on 17 rice grain samples harvested 96-115 days after a single post-emergence application to dry seeded rice with the 4 lb/gal EC formulation (alone or tank-mixed with propanil) at 0.75-2 lb ai/A (0.75x-2x the maximum registered rate); both ground and aerial equipment were used for application and the rice fields were flooded 2-41 days posttreatment. Pendimethalin residues were nondetectable (<0.05 ppm) -0.07 in or on seven rice straw samples treated as described above; the occurrence of detectable residues is of no concern since the use of rice straw for livestock feed is not permitted.

Adequate electron capture GC methods were used for residue quantitation (M-444.1). The test states of AR (38%), LA (14%), MS (8%), and TX (15%) provide adequate geographic representation since collectively they produced 75% of the 1981 U.S. rice crop (Agricultural Statistics, 1982, p. 21).

No data were submitted pertaining to residues of CL 202,347 in or on rice grain, although the established 0.05 ppm tolerance includes both pendimethalin per se and its metabolite CL 202,347. Since the validated limit of detection of these compounds in rice grain is each 0.05 ppm, we recommend that the tolerance for their combined residues be increased to 0.1 ppm. Marei, et al. (1974) conducted a study with rice plants which showed that total [^{14}C]pendimethalin equivalents in rice seed were 0.05 ppm following a treatment equivalent to 3 lb ai/A (3x the registered rate); the ^{14}C equivalents were not characterized (for details, refer to Nature of the Residue in Plants section). This study, coupled with field trials which showed nondetectable (<0.1 ppm) combined residues in or on corn or sorghum grain, supplies adequate supportive evidence that combined residues of pendimethalin and its metabolite CL 202,347 will not exceed 0.1 ppm in or on rice grain; we recommend that the established 0.05 ppm tolerance be increased to 0.1 ppm.

Sorghum grain

Tolerance:

A tolerance of 0.1 ppm has been established for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sorghum grain (40 CFR 180.361).

Use directions and limitations:

The 4 lb/gal EC formulation has been registered for use on sorghum at 0.5-1.5 lb ai/A (exact rate is dependent upon soil texture, whether the formulation is used alone or tank mixed, and if the use site is located in either the southern or northern U.S.). A single annual, postemergence, incorporated application may be made using ground equipment from the 4-inch stage of growth up to the last cultivation (layby). This formulation may be tank mixed with atrazine. Treatment may not be made on peat or muck soils, nor may a tank mixed application with atrazine be made on coarse textured soils (sands, loamy sands, and sandy loams). Treated forage may be grazed by or fed to livestock 21 days after application.

Conclusions:

Sufficient data are available to assess the adequacy of the established tolerance and label directions. No additional data are required for this commodity.

The established tolerance and label directions are found to be adequate. No Canadian or Mexican tolerance or Codex MRL exists for pendimethalin residues in or on sorghum grain.

References (used):

American Cyanamid Co. 1982. Registration application for use of PROWL® herbicide as a CULTI-SPRAY™ (postemergence incorporated) treatment in grain sorghum. Report Nos. C-1779, C-1784, and C-1785. Submitted under EPA Reg. No. 241-243. (Accession No. 248325).

American Cyanamid Co. 1979. Residue analysis of Prowl or Atrazine in grain sorghum. Report Nos. C-1571, C-1572, C-1573, C-1578, C-1579, C-1580, C-1581, C-1582, C-1583, and C-1584. Compilation; unpublished study received August 14, 1979 under 241-243. (CDL:098918-A; MRID:00106807).

American Cyanamid Co. 1976. Residues of Prowl herbicide in sorghum. Report Nos. C-1053, C-1056, C-1061, and C-1062. Compilation; unpublished study received January 6, 1978 under 241-EX-88. (CDL:096712-A; MRID:00106791).

Discussion of the data:

Residue data were submitted by American Cyanamid Co. (MRID Nos. 00106791 and 00106807 and Accession No. 248325) involving pendimethalin residues in or on sorghum grain from 23 tests conducted in AR (1), CA (1), CO (1), KS (2), LA (1), NE (3), NM (2), SD (1), TX (10), and VA (1). The combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite were nondetectable at <0.1 ppm (includes pendimethalin and its metabolite at <0.05 ppm each) in or on 29 grain samples 57-144 days following a postemergence application (incorporated or nonincorporated) with the 4 lb/gal EC formulation at 0.75-2 lb

ai/A (0.5x- 1.3x the maximum use rate); four of these grain samples reflect a preemergence application at 1.5-2 lb ai/A (1x-1.3x; currently not a registered use), and six of the samples reflect use of the 4 lb/gal EC tank-mixed with either atrazine or milogard. Ground equipment was used for all applications.

Adequate GC methods (Method Nos. M-744 and M-746) were used for data collection. Geographic representation was adequate because the states of AR (2%), CA (1%), CO (1%), KS (27%), LA (<1%), NE (19%), NM (1%), SD (2%), TX (31%), and VA (<1%), which were used as test sites, produced approximately 84% of the total 1981 U.S. crop of sorghum grain (Agricultural Statistics, 1982, p. 52; preliminary statistics); the percent of contribution to the total U.S. sorghum grain production by each state is parenthesized. Data were not submitted involving the processed products of sorghum grain (milled products); however, because all residue levels were nondetectable (<0.1 ppm) in the grain data submitted and residues are not expected to concentrate in milled products, we feel the submission of such data to be unnecessary. We conclude therefore, that the available data are adequate and that the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sorghum grain are not expected to exceed the established tolerance.

Wheat grain

Tolerance:

A tolerance of 0.1 ppm has been proposed by American Cyanamid Co. (1983, PP# 3F2788) for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on wheat grain and is currently pending.

Use directions and limitations:

The 4 lb/gal EC formulation has been proposed for use on wheat at 1.5 lb ai/A as a preemergence treatment made using either ground or aerial equipment; spring treatments may be incorporated before crop emergence (EPA memorandum from R. Perfetti [RCB/HED] to R. Taylor [FHB,RD] and Toxicology Branch dated March 9, 1983; in correspondence file of PP#3F2788).

Conclusions:

Available data in support of the proposed tolerance for pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on wheat grain are currently under review. Therefore, the adequacy of the data cannot be assessed at the present time. No Canadian or Mexican tolerances or Codex MRL exist for pendimethalin residues in or on wheat grain.

References:

N/A.

Discussion of the data:

N/A.

Forage, Fodder, and Straw of the Cereal Grains Group

Conclusions for the Forage, Fodder and Straw of the Cereal Grains Group:

A crop group tolerance is not appropriate at the present time for the following reason:

- Currently proposed tolerances for two representative members (sweet corn and wheat) of this crop group are pending; forage and fodder tolerances have been established for two other representative members (field corn and sorghum). When and if the currently pending tolerances are established, a crop group tolerance should be considered at that time.

Barley forage and straw

Tolerance:

A tolerance of 0.1 ppm has been proposed by American Cyanamid Co. (1983, PP# 3F2788) for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on both barley forage and barley straw and is currently pending for each.

Use directions and limitations:

The 4 lb/gal EC formulation has been proposed for use on barley at 1.5 lb ai/A as a preemergence treatment made using either ground or aerial equipment (EPA memorandum from R. Perfetti [RCB/HED] to R. Taylor [FHB/RD] and Toxicology Branch in correspondence file of PP# 3F2788, dated March 9, 1983).

Conclusions:

Available data in support of the proposed tolerances for pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on barley forage and straw are currently under review. Therefore, the adequacy of the data cannot be assessed

at the present time. No Canadian or Mexican tolerances or Codex MRL exist for pendimethalin residues in or on barley forage or straw.

References:

N/A.

Discussion of the data:

N/A.

Corn (field) forage and fodder

Tolerance:

Tolerances have been established for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on field corn forage and fodder at 0.1 ppm (40 CFR 180.361).

Use directions and limitations:

The 10% G, 3 lb/gal EC, 4 lb/gal EC, and 60% DG (dispersible granules) formulations have been registered for use on field corn at 0.75-2 lb ai/A as a preemergence application (broadcast or band) made after planting before weeds and crop emerge using ground equipment; the 4 lb/gal EC and 60% DG may be applied using aerial equipment. The 10% G and 3 lb/gal EC formulations are not to be used on sands or loamy sands or on soils containing <1.5% organic matter.

The 4 lb/gal EC has been registered for an early postemergence application (broadcast or band) at 1-1.5 lb ai/A (tank mixed with atrazine or cyanazine WP formulations) using ground equipment or aerial equipment; application is to be made no later than the 2-leaf growth stage and when weeds are ≤1 inch tall and may not follow a preemergent pendimethalin application. This same formulation may be used as a postemergence incorporated treatment at 0.5-1.5

lb ai/A using ground equipment from the 4-inch growth stage up to the last cultivation. Several uses involve tank mixes with other herbicides. Treated forage may not be fed to, or grazed by, livestock until 21 days after treatment.

The states of CO (EPA SLN No. CO-0790014), KS (EPA SLN No. KS-790009), NE (EPA SLN No. NE-790007), and TX (EPA SLN No. TX-780018) have been issued state label registrations under Section 24(c) for use of the 4 lb/gal EC formulation on field corn at 0.75-1.5 lb ai/A as a postemergence incorporated application used alone or tank mixed with atrazine and applied with ground equipment.

Conclusions:

The available data are adequate to support the label directions and the established tolerances for pendimethalin residues in or on field corn forage and fodder. No additional data are required for these commodities. No Codex MRL or Canadian or Mexican tolerance has been established.

Note:
Additional metabolism studies are required. If new metabolites of residue concern are found, then additional field residue studies for field corn may be needed.

References (used):

American Cyanamid Co. 1981. Residues of Prowl. Report Nos. C-1327, C-1328, C-1495, C-1496, C-1497, C-1498, C-1499, C-1891, C-1895, and C-1896. Compilation; unpubished study, including published data, submitted under EPA Reg. No. 241-243. (CDL:246583-A; MRID 00093697).

American Cyanamid Co. 1978. Amounts of residues of Prowl, its metabolite (CL 202,347), Atrazine, and Bladex in or on field corn. Report Nos. C-874, C-899, C-900, C-903, C-1064, C-1336, C-1337, C-1341, C-1342, C-1343, and C-1344. Compilation; unpublished study submitted under EPA Reg. No. 241-243. (CDL:233898-A; MRID 00106820).

Bodnarchuk, D., Laporta, M., Potts, C., et al. 1975. Summary--Prowl and Banvel--residues in corn plants. Report Nos. C-869, C-875, C-876, C-877, and C-878. Unpublished study submitted by American Cyanamid Co. under EPA Reg. No. 241-243. (CLD:230428-A; MRID 00030693).

Bodnarchuk, Wyckoff, J.C., Nzewi, G.I. 1974. Prowl (CL 92,553): Determination of CL 92,553...and CL 202,347...residues in field corn tissues: Report

No. C-450. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-M; MRID 00023788).

Moyer, M., Potts, C., Bodnarchuk, D., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., and Atrazine...and Bladex... residues in field corn tissues: Report No. C-461. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-P; MRID: 00023791).

Moyer, M., Potts, C., Wyckoff, J.C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...residues in field corn tissues: Report No. C-463. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-Q; MRID:00023792).

Moyer, M., Potts, C., Wyckoff, J.C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-464. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-R; MRID:00023793).

Wyckoff, J.C., Bodnarchuk, D., Moyer, M., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in corn tissues: Report No. C-456. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-N; MRID:00023789).

Wyckoff, J.C., Bodnarchuk, D., Moyer, M., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553...and CL 202,347...residues in field corn tissues: Report No. C-459. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-L; MRID:00023787).

Wyckoff, J.C., Bodnarchuk, D., Moyer, M., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-466. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474; MRID:00023795).

Wyckoff, J.C., Moyer, M., Bodnarchuk, D., et al. 1973. Prowl (CL 92,553): Determination of CL 92,553...CL 202,347...Atrazine...and Bladex...residues in field corn tissues (fodder and grain): Report No. C-401. Unpublished study

received under PP# 4G1451; submitted by American Cyanamid Co. (CDL:093869-0; MRID:00029029).

Wyckoff, J.C., Bodnarchuk, D., Nzewi, G.I. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-460. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-0; MRID:00023790).

Wyckoff, J.C., Bodnarchuk, D., Potts, C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553...and CL 202,347...residue in field corn tissues (grain and forage): Report No. C-457. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-K; MRID:00023786).

Wyckoff, J.C., Bodnarchuk, D., and W.S. Van Scoik. 1973. Prowl (CL 92,553): Determination of CL 92,553 [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] and CL 202,347 [4-([1-ethylpropyl]amino)-2-methyl-3,5-dinitro-benzyl alcohol] residues in field corn plants. Report No. C-382 submitted by American Cyanamid Co. under PP# 4G1451. (CDL:093869-N; MRID:00029028).

Wyckoff, J.C., Moyer, M., Potts, C., et al. 1974. Prowl (CL 92,553): Determination of CL 92,553..., CL 202,347..., Atrazine...and Bladex...residues in field corn tissues: Report No. C-465. Unpublished study received under PP# 5F1556; submitted by American Cyanamid Co. (CDL:094474-S; MRID:00023794).

Discussion of the data:

Residue data were submitted by American Cyanamid Co. (MRID Nos. 00093697, 00106820, 00023786, 00023790, 00023789, 00029029, 00023788, 00023787, 00023793, 00023791, 00029028, 00023795, 00023794, 00023792, and 00030693) involving pendimethalin residues in or on field corn forage, fodder, silage, and stover; tolerances currently exist for forage and fodder only. The submitted data on field corn fodder involved 48 tests conducted in CO (6), IA (6), IL (4), KY (2), MN (4), MO (1), NE (5), NY (9), OH (5), SD (4), and WI (2) and on field corn forage involved 9 tests conducted in IL (5), OH (1), and MN (3). Data were submitted involving field corn silage from 76 tests conducted in CA (1), CO (10), IA (6), IL (8), IN (1), MO (1), MN (9), NE (13), NY (10), OH (5), SD (4), TX (6), and WI (2) and data were submitted involving stover from 10

tests conducted in CO (4), KS (4), and NE (2). The number of tests conducted in each state is parenthesized. The combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite were nondetectable at <0.1 ppm (includes pendimethalin and its metabolite at <0.05 ppm each) in or on 18 samples of forage, 54 samples of fodder, 144 samples of silage, and 10 samples of stover. Exceptions were found in two samples of silage which contained apparent pendimethalin at 0.063 and 0.105 ppm (the 3,5-dinitrobenzyl alcohol metabolite was nondetectable at <0.05 ppm); the corresponding control sample contained pendimethalin at 0.013 ppm. In view of the nondetectable residues contained in all other silage samples, treated and control, we believe these two values to be aberrant.

Treatment regimes included the use of the 4 lb/gal EC at 0.75-2 lb ai/A (0.38-1x the maximum registered use rate) as a preemergence or postemergence application with or without incorporation applied alone or tank mixed with either atrazine, cyanazine, or dicambra using ground equipment and sampling intervals of 96-172 days for fodder, 67-116 days for silage, and 97-122 days for stover. Some samples were from plots treated preemergence or preplant prior to the pendimethalin application with either atrazine, Eradicane, Sutan, or atrazine plus alachlor. Using aerial equipment, this same formulation was applied postemergence (plants were 8-10 inches tall) and incorporated at 1 lb ai/A (0.5x), and after 53 and 108 days two samples each of silage and stover; respectively, were collected. The 3 lb/gal EC was used in a preemergence application at 1.5-6 lb ai/A (0.75-3x) using ground equipment and sampling intervals of 125-174 days for fodder, 35-60 days for foliage, and 78-112 days for silage; this formulation was also applied alone or tank mixed with either atrazine or cyanazine.

Data were also submitted involving 12 samples each of popcorn fodder and silage from eight tests conducted in IL and IN (Report Nos. C-869 and C-875 in MRID No. 00030693) and all of the samples contained nondetectable (<0.1 ppm) residues following a preemergence application of the 4 lb/gal EC at 1.5-2 lb ai/A and sampling intervals of 57-71 days for silage and 129-135 days for fodder. No tolerance currently exists for pendimethalin residues in or on popcorn and these data have been presented for general information purposes only.

The available data did not involve the use of the 10% G or 60% DG formulations (also registered for use on field corn) as test substances, however, because all residue values involving forage and fodder were nondetectable as the result of the application of the 3 lb/gal EC or 4 lb/gal EC, we feel additional data are not necessary. Adequate GC methods (Method Nos. M-458.1 and M-459.1) employing electron capture detection were used for data collection. Geographic representation was adequate because the states of IL, IA, MN, MO, OH, and WI in which tests involving forage and fodder were conducted represent the corn belt states which is the major U.S. production region of corn.

We conclude that the available data are adequate and that the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on field corn forage and fodder are not expected to exceed the established tolerance following the registered use method.

Note:
Additional metabolism studies are required. If new metabolites of residue concern are found, then additional field residue studies for field corn may be needed.

Corn (sweet) forage and fodder

Tolerances:

Tolerances have been proposed by American Cyanamid Co. (1982, PP# 2F2628) for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sweet corn forage and fodder at 0.1 ppm and are currently pending.

Use directions and limitations:

The 4 lb/gal EC formulation has been proposed for use on sweet corn (processing varieties only) at 0.75-2 lb ai/A as a preemergence or postemergence (no later than the 2-leaf growth stage) treatment used alone or tank mixed with atrazine or cyanazine in MN and WI only. Air or ground equipment may be used for application [EPA memorandum from A. Smith (RCB) to R. Taylor (Registration Division) in correspondence file of PP# 2F2628].

Conclusions:

Available data in support of the proposed tolerances for pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sweet corn forage and fodder are currently under review. Therefore, the adequacy of the data cannot be assessed at the present time. No Canadian or Mexican tolerances or Codex MRL exist for pendimethalin residues in or on sweet corn forage and fodder.

References:

N/A.

Discussion of the data:

N/A.

Sorghum forage and fodder

Tolerances:

Tolerances of 0.1 ppm have been established for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sorghum forage and fodder (40 CFR 180.361).

Use directions and limitations:

The 4 lb/gal EC formulation has been registered for use on sorghum at 0.5-1.5 lb ai/A (exact rate is dependent upon soil texture, whether the formulation is used alone or tank mixed, or if the use site is located in either the southern or northern U.S.). A single annual postemergence, incorporated application may be made using ground equipment from the 4-inch stage of growth up to the last cultivation (layby). This formulation may be tank mixed with atrazine. Treatment may not be made on peat or muck soils, nor may a tank mixed application with atrazine be made on coarse textured soils (sands, loamy sands, and sandy loams). Treated forage may be grazed by or fed to livestock 21 days after application.

Conclusions:

Sufficient data are available to support the established tolerance and label directions. No additional data are required for this commodity.

Additional metabolism studies are required. If new metabolites of residue concern are found, then additional field residue studies for sorghum will be needed.

The established tolerance and label directions are found to be adequate. No Canadian or Mexican tolerance or Codex MRL exists for pendimethalin residues in or on sorghum forage and fodder.

References (used):

American Cyanamid Co. 1982. Registration application for use of PROWL® herbicide as a CULTI-SPRAY™ (postemergence incorporated) treatment in grain sorghum. Report Nos. C-1779, C-1784, and C-1785. Submitted under EPA Reg. No. 241-243. (Acession No. 248325).

American Cyanamid Co. 1979. Residue analysis of Prowl or Atrazine in grain sorghum. Report Nos. C-1571, C-1578, C-1579, C-1580, C-1581, C-1582, C-1583, and C-1584. Compilation; unpublished study received August 14, 1979 under 241-243. (CDL:098918-A; MRID 00106807).

American Cyanamid Co. 1976. Residues of Prowl herbicide in sorghum. Report Nos. C-1053, C-1056, C-1058, C-1059, C-1060, C-1061, and C-1062. Compilation; unpublished study received January 6, 1978 under 241-EX-88. (CDL:096712-A; MRID 00106791).

Discussion of the data:

Residue data were submitted by American Cyanamid Co. (MRID Nos. 00106791 and 00106807) involving pendimethalin residues in or on sorghum fodder from five tests conducted in TX; sorghum forage from four tests conducted in KS; and two tests conducted in TX. Data were also submitted involving sorghum silage from 14 tests conducted in CO (4), KS (2), NE (2), NM (2), and TX (4) involving sorghum straw from three tests conducted in CA (1), LA (1), and SD (1), and involving sorghum stover from 10 tests conducted in CO (1), NE (2), NM

(2), and TX (5) [the number of tests per state is parenthesized]. The combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite were nondetectable at <0.1 ppm (includes pendimethalin and its metabolite at 0.05 ppm each) in or on five samples of fodder, six samples of forage, 18 samples of silage, three samples of straw, and 14 samples of stover. One sample of forage was an exception and contained pendimethalin per se slightly higher than the detection limit at 0.055 ppm (the metabolite was nondetectable at <0.05 ppm), however, this value is apparently uncorrected for the control sample and percent recovery (control values were not provided). We therefore believe this value to be aberrent. Treatment was made using the 4 lb/gal EC formulation as a postemergence application (incorporated or non-incorporated) at 0.75-2 lb ai/A (0.5-1.3x the maximum registered use rate) or as a preemergence application at 1.5-2 lb ai/A (1x-1.3x; currently not a registered use; of the previously mentioned totals, this involved four samples of fodder, two samples of forage, and three samples of silage). Seven silage samples, three stover samples, three forage samples, and two fodder samples involved a tank mix application with either atrazine or propazine. Sampling intervals used for data collection for fodder ranged from 107 to 144 days, for forage 88 to 139 days, for silage 41 to 105 days, for straw 93 to 120 days, and for stover 57 to 98 days. Ground equipment was used for all applications.

Adequate GC methods (Method Nos. M-743 and M-745) were used for data collection and tests were conducted with adequate geographic representation because the states of KS and TX, which were used as test sites for forage and fodder data, respectively contribute 28 and 29% to the total U.S. acreage harvested for sorghum forage and the state of KS alone produces 38% of the total U.S. sorghum crop for silage (Agricultural Statistics, 1982, p. 52). We conclude that the available data are adequate and that the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on sorghum forage and fodder are not expected to exceed the established tolerances.

Additional metabolism studies are required. If new metabolites of residue concern are found, then additional field residue studies for sorghum forage will be needed.

Wheat forage and straw

Tolerances:

A tolerance of 0.1 ppm has been proposed by American Cyanamid Co. (1983, PP# 3F2788) for the combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on both wheat forage and wheat straw and is currently pending for each.

Use directions and limitations:

The 4 lb/gal EC formulation has been proposed for use on wheat at 1.5 lb ai/A as a preemergence treatment made using either ground or aerial equipment; spring treatments may be incorporated before crop emergence (EPA memorandum from R. Perfetti [RCB/HEC] to R. Taylor [FHB/RD] and Toxicology Branch dated March 9, 1983; in correspondence file of PP# 3F2788).

Conclusions:

Available data in support of the proposed tolerances for pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite in or on wheat forage and straw are currently under review. Therefore, the adequacy of the data cannot be assessed at the present time. No Canadian or Mexican tolerances or Codex MRL exist for pendimethalin residues in or on wheat forage or straw.

References:

N/A.

Discussion of the data:

N/A.

MISCELLANEOUS COMMODITIES

Cottonseed

Tolerance:

A tolerance of 0.1 ppm has been established for the combined residues of pendimethalin and its metabolite (CL 202,347) in or on cottonseed (40 CFR 180.361).

The 3 and 4 lb/gal EC and the 60% dispersible granule (DG) formulations are registered for use on cotton at 0.5-1.5 lb ai/A as a single preplant incorporated application using ground or aerial equipment. The 4 lb/gal EC is also registered for preplant incorporated treatments at 1-2 lb ai/A in all states except AZ, CA, and NM or in soils with >3% organic matter. The 4 lb/-gal EC may also be applied at 0.5-1.5 lb ai/A as a preemergence treatment in all states except in AZ, CA, NM, OK, and TX using ground equipment immediately after planting (this treatment is not soil-incorporated). Where specified, soil incorporation is conducted within 7 days after treatment prior to planting. Several uses allow tank mixes with other herbicides. Livestock may not graze in, or consume forage from, treated cotton fields.

Conclusions:

The available data partially support the established tolerance for pendimethalin residues in or on cottonseed and are sufficient to determine that the label directions are adequate. Residues were not adequately determined in processed products. Additional processing data may be required for this commodity and will be translated from the requested soybean processing study (see p. 61). No Codex MRL or Canadian or Mexican tolerance exists for pendimethalin residues in or on cottonseed.

References (used):

American Cyanamid Co. 1974. Extent of PROWL herbicide and its metabolite residues--cotton plants, seed, oil, meal and in milk, including a description of the analytical methods used. Compilation; [includes Report Nos. C-533, C-534, C-485-489, and C-491-496] unpublished study received on unknown date under PP#5G1567. (CDL:094284-A; MRID:00106752).

American Cyanamid Co. 1978. Residues of PROWL herbicide. Compilation; [includes Report Nos. C-1456 and C-1457] unpublished study received Aug. 14, 1979 under 241-243. (CDL:238944-B; 241020; MRID:00106829).

Smith, J., Lignowski, E., Coble, H.D., et al. 1978. Summary: PROWL (CL 92,553) plus Cotoran (fluometuron) preemergence tank mixture--soil and cottonseed residues [includes Report Nos. C-1348, 1349, and 1350]. Unpublished study received Sep. 11, 1978 under 241-243; submitted by American Cyanamid Co. (CDL:235084-B; MRID:00018997).

Discussion of the data:

American Cyanamid Co. (MRIDs 00106752, 00106829, and 00018997) submitted data pertaining to residues of pendimethalin per se and its metabolite CL 202,347 in or on cotton foliage and cottonseed from the following test locations (the number of tests/state is given parenthetically): AZ (9), AR (2), CA (6), LA (3), MS (6), MO (2), NC (2), and TX (6). All samples received a single, preemergence (at-planting) or preplant incorporated application with the 3 or 4 lb/gal EC formulation (alone or tank-mixed with prometryn or fluometuron) at 0.5-2.5 lb ai/A (0.25-1.25x the maximum registered rate); applications were made using both ground and aerial equipment. Combined residues in or on 47 cotton foliage samples harvested 27-219 days after treatment were nondetectable (<0.1 ppm, including pendimethalin per se and CL 202,347 each at <0.05 ppm). Two determinations on one additional sample harvested 28 days after a preemergence at-plant treatment at 1 lb ai/A yielded combined residues of <0.109 ppm [including pendimethalin per se at 0.059 ppm and CL 202,347 at <0.05 ppm (nondetectable)] and <0.111 ppm [including pendimethalin per se at 0.061 ppm and

CL 202,347 at <0.05 ppm (nondetectable)]. Combined residues in or on 36 cottonseed samples harvested 133-284 days following treatment were nondetectable (<0.1 ppm, including pendimethalin per se and CL 202,347 each at <0.05 ppm).

Data pertaining to pendimethalin residues in oil and meal produced from cottonseed were also submitted by American Cyanamid Co. Cottonseed bearing nondetectable combined residues (<0.1 ppm, including pendimethalin per se and CL 202,347 each at <0.05 ppm) resulting from treatment with the 3 lb/gal EC formulation at 1-2.5 lb ai/A (0.5-1.25x) were processed into cottonseed oil and meal (Report Nos. C-492, C-496, and C-485I; MRID 00106752). Combined residues in solvent-extracted crude oil (three samples) and meal (one sample) were also nondetectable (<0.1 ppm, including pendimethalin per se and CL 202,-347 each at <0.05 ppm). These processing studies are not adequate because the cottonseed did not contain detectable residues. We feel that pendimethalin residues have a propensity to concentrate in oil based on the fact that hexane efficiently extracts these residues from oil seeds (see Tables 2 and 3 of the Residue Analytical Methods section).

Adequate electron capture GC methods were used for residue quantitation for the following commodities: cotton foliage (M-516 and M-517), cottonseed (M-476.1) and M-523), cottonseed oil (M-514 and M-515), and cottonseed meal (M-524 and M-525). Adequate geographic representation is provided by AR (4%), AZ (4%), CA (11%), LA (5%), MS (9%), MO (2%), and TX (52%) since these states collectively produce 87% of the total U.S. cotton crop (Agricultural Statistics, 1982, p. 62). In our opinion, the available data are adequate to support the numerical value of the established tolerance (0.1 ppm) for pendimethalin residues in or on cottonseed. However, the submitted processing data are insufficient to demonstrate that pendimethalin residues do not concentrate in cottonseed processed fractions; therefore, additional data may be required.

Additional metabolism data are requested. Depending on the results of these data, additional processing studies for soybeans may be requested. Due to the fact that residues in seed crops may concentrate during processing to oil to the extend of 6x for soybeans and as much as 25x for corn, there is a concern that combined residues of pendimethalin and CL 202,347 in processed oil may exceed the established tolerance of 0.1 ppm for the individual raw agricultural commodity. Since additional metabolism studies are requested, the request for an additional processing study for soybeans will depend upon the results of the final residues of concern. If requested, this processing study will be translated to cottonseed.

Peanuts

Tolerances:

Tolerances of 0.1 ppm have been established for the combined residues of pendimethalin and its metabolite (CL 202,347) in or on peanuts, peanut hay, and peanut forage. Also, a tolerance of 0.25 ppm has been established for the combined residues of pendimethalin and its metabolites CL 202,347 and CL 217,146 in or on peanut hulls [40 CFR 180.361(a) and (b)].

Use directions and limitations:

The 4 lb/gal EC formulation is registered for use on peanuts at 0.5-0.75 lb ai/A in NM, OK, and TX and at 0.75-1 lb ai/A elsewhere. A single, annual preplant application (broadcast or band) is made using aerial or ground equipment up to 60 days preplant; incorporation should be into the top 1-2 inches of soil within 7 days of application. Tank mixes with vernam may be applied.

Conclusions:

The available data support the established tolerances for pendimethalin residues in or on peanut hulls and peanut forage and partially support the tolerance for residue in or on peanuts. Additional processing data may be required. Additional metabolism data are requested. Depending on the results of these data, additional processing studies for soybeans may be requested. Due to the fact that residues in seed crops may concentrate during processing to oil to the extend of 6x for soybeans and as much as 25x for corn, there is a concern that combined residues of pendimethalin and CL 202.347 in processed oil may exceed the established tolerance of 0.1 ppm for the individual raw agricultural commodity. Since additional metabolism studies are requested, the request for an additional processing study for soybeans will depend upon the results of the final residues of concern. If requested, this processing study will be translated to peanuts.

Note that the presently established tolerance for combined residues of pendimethalin per se and its metabolites CL 202,347 and CL 217,146 has been questioned (see EPA memorandum by R. Perfetti, dated Sept. 9, 1983; in correspondence file of PP# 3F2788). A decision regarding the appropriate tolerance expression should await the results of the requested plant metabolism data.

No data are available to support the tolerance for peanut hay. Due to the fact that no detectable residues were found for pendimethalin and its CL 202.347 metabolite, (<0.05 ppm) in peanut forage treated at exaggerated rates 31-153 days after application, it is our opinion that similarly no detectable residues (<0.05 ppm) of either compound will occur in peanut hay and that no additional residue data are needed.

There is no Canadian or Mexican tolerance, nor is there a Codex MRL for pendimethalin in or on peanuts, peanut forage or peanut hay.

References (used):

Smith, J., Lignowski, E.M., Goddard, G., et al. 1979. PROWL® pendimethalin (CL 92,553/4E): Residues of CL 92,553, CL 202,347 and CL 217,146 in peanut hulls: Report No. C-1628. Unpublished study received Apr. 29, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:099395-F; MRID 00031217).

Smith, J., Lignowski, E.M., Dunn, J.C., et al. 1979. PROWL® pendimethalin (CL 92,553/4E): Residues of CL 92,553, CL 202,347 and CL 217,146 in peanut hulls: Report No. C-1620. Unpublished study received Apr. 29, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:099395-D; MRID 00031215).

Smith, J., Lignowski, E.M., Walls, F.R., Jr., et al. 1979. PROWL® pendimethalin (CL 92,553/4E): Residues of CL 92,553, CL 202,347 and CL 217,146 in peanut hulls: Report No. C-1631. Unpublished study received Apr. 29, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:099395-E; MRID 00031216).

American Cyanamid Co. 1975. Extent of PROWL herbicide and its metabolite residues in peanut foliage, hulls, nuts, oil and meal, inlcuding a description of the analytical methods used. Compilation [includes Reports Nos. C-669 through C-677]; unpublished study received Feb. 9, 1976 under PP# 6F1741. (CDL:094960-A; MRID 00106785).

Discussion of the data:

Residue data were submitted by American Cyanamid Co. (MRID 00106785) from tests conducted in AL (1), GA (2), NC (4), TX (2), and VA (5); the number of tests per state is given parenthetically. Combined residues of pendimethalin and its metabolite (CL 202,347) were nondetectable (<0.1 ppm, including pendimethalin per se and CL 202,347 each at <0.05 ppm) in or on 13 peanut samples harvested 92-155 days following a single preplant, soil-incorporated application with the 3 lb/gal EC formulation at 0.75-1.5 lb ai/A (1-1.5x the maximum registered rate). Combined residues were also nondetectable in or on 26 peanut foliage samples harvested 31-153 days and 13 peanut hull samples harvested 92-155 days after the same treatment; two additional hull samples from a VA test site (Report No. C-677) yielded combined residues (average of two determinations per sample) of <0.11 ppm [including pendimethalin per se at <0.065 ppm and CL 202,347 at <0.05 ppm (ND)] to 0.14 ppm (including pendimethalin per se at 0.090 ppm and CL 202,347 at 0.055 ppm). Field-weathered peanut nutmeat samples (Report Nos. C-670 and C-677) containing nondetectable combined residues (<0.1 ppm) were processed into oil and meal; combined residues in two samples each of peanut oil and meal were also nondetectable (<0.1 ppm, including pendimethalin per se and CL 202,347 each at <0.05 ppm). These processing studies are inadequate because peanuts did not contain detectable residues. We feel that pendimethalin residues have a propensity to concentrate in oil as evidenced by the efficiency with which hexane extracts these residues from oil seeds (see Tables 2 and 3 of the Residue Analytical Methods section). No data were submitted pertaining to residues of pendimethalin in or on peanut hay.

American Cyanamid Co. (MRIDs 00031217, 00031215, and 00031216) also submitted data pertaining to combined residues of pendimethalin per se and its metabolites CL 202,347 and CL 217146 in or on peanut hulls from tests conducted in AL (3), NC (2), and NM (1); the number of tests/state is given parenthetically. Combined residues in or on six peanut hull samples harvested 140-192 days following either a single preplant incorporated application at 0.75-2 lb ai/A (1.3-2x) or one preplant application followed by an at-cracking or postemergence application at 0.75-1 lb ai/A (multiple or postemergence use on peanuts is not presently registered) were <0.20 to <0.25 ppm [including pendi-

methalin per se at <0.05 ppm (ND)-0.1 ppm, CL 202,347 at <0.05 ppm (ND)-0.06 ppm, and CL 217,146 at <0.1 ppm (ND)]. Although the metabolite CL 217,146 is presently included in the 0.25 ppm tolerance for pendimethalin residues in or on peanut hulls, EPA has recommended that the present regulation for this commodity be deleted and that the tolerance be established in terms of pendimethalin per se plus its metabolite CL 202,347 only (see EPA memorandum by R. Perfetti, dated Sept. 9, 1983; in correspondence file of PP# 3F2788). Therefore, we report here that combined residues of pendimethalin per se and its metabolite CL 202,347 in or on the above-described peanut hull samples were <0.10 to <0.15 ppm [including pendimethalin per se at <0.05 (ND)-0.1 ppm and CL 202,347 at <0.05 (ND)-0.06 ppm]. Since the terminal residues of pendimethalin have not been adequately defined in plants (see Nature of the Residue in Plants section), we recommend that a decision pertaining to the residues of concern in or on peanut hulls be made upon receipt of the requested plant metabolism data.

Adequte electron capture GC methods were not used for residue quantitation of pendimethalin per se and its CL 202,347 metabolite in or on the following commodities (method designation numbers are given parenthetically): peanuts (M-577 and M-579), peanut hulls and foliage (M-578 and M-580) peanut meal (M-592 and M-593), and peanut oil (M-590 and M-591). Residue quantitation of the pendimethalin metabolite CL 217,146 was also accomplished with an adequate electron capture GC method (M-1029). Adequate geographic representation is provided by AL (15%), GA (41%), NC (14%), TX (10%), and VA (8%), since these states collectively produced 88% of the total U.S. peanut crop in 1981 (Agricultural Stastics, 1982, p. 126).

In our opinion, the available data are adequate to support the numerical value of the established 0.1 ppm tolerance for peanuts and peanut forage and the currently established 0.25 ppm tolerance for peanut hulls (see above discussion regarding the appropriate tolerance definition); however, no data were presented to support the established hay tolerance. Due to the fact that no detectable residues were found for either compound (<0.05 ppm) in peanut forage treated at exaggerated rates 31-153 days after application, it is our opinion that a similar situation exists for peanut hay and that no additional residue data for peanut hay is requested. The submitted processing data are insufficient to demonstrate that pendimethalin residues do not concentrate in peanut processed fractions; therefore, additional data may be required. For particular see p. 61.

Safflower seed

Tolerance:

A tolerance has not been established for residues of pendimethalin in or on safflower seed because the data in support of this proposed tolerance are currently under review. A tolerance of 0.1 ppm has been proposed for residues of pendimethalin *per se* and its metabolite (CL 202,347) in or on safflower seed (1983, PP# 3F2844).

Use directions and limitations:

The 4 lb/gal EC formulation is proposed for preplant, soil-incorporated use on safflower at 0.5-1.5 lb ai/A, depending upon soil characteristics. This proposed use pattern was obtained from an EPA memorandum by K.H. Arne, dated July 6, 1983 (in correspondence file for PP# 3F2844).

Conclusions:

The available data in support of the proposed tolerance for residues of pendimethalin *per se* and its metabolite (CL 202,347) are currently under review. There is no Canadian or Mexican tolerance, nor is there a Codex MRL for pendimethalin residues in or on safflower seed.

References:

N/A.

Discussion of the data:

N/A.

Sugarcane

Tolerance:

A tolerance has not been established for residues of pendimethalin in or on sugarcane because the data in support of this proposed tolerance are currently under review. A tolerance of 0.1 ppm has been proposed for residues of pendimethalin per se and its metabolite (CL 202,347) in or on sugarcane (1983, PP# 3F2765).

Use directions and limitations:

The 4 lb/gal EC formulation is proposed for use on sugarcane (plant or ratoon crop) at 1-2 lb ai/A. Two applications per season are proposed: an aerial or ground, preemergence application (band or broadcast) is soil incorporated, either mechanically or by rainfall, and is followed by a directed spray application (ground equipment only) made at layby. Livestock may not graze pendimethalin-treated fields or be fed treated forage or fodder.

Conclusions:

The available data in support of the proposed tolerance for residues of pendimethalin per se and its metabolite (CL 202,347) are currently under review. There is no Canadian or Mexican tolerance, nor is there a Codex MRL for pendimethalin residues in or on sugarcane.

References:

N/A.

Discussion of the data:

N/A.

Sunflower seed

Tolerance:

A tolerance of 0.1 ppm has been established for residues of pendimethalin and its metabolite (CL 202,347) in or on sunflower seed (40 CFR 180.361).

Use directions and limitations:

The 4 lb/gal EC formulation is registered for use on sunflower at 0.5-1.5 lb ai/A, depending upon soil characteristics. A preplant incorporated application (broadcast or band) is to be made once per year; application may be made with ground or aerial equipment. Livestock may not graze or be fed forage from treated sunflower fields. Tank mixes with chloramben or a sequential preemergence application of chloramben may be applied.

Conclusions:

The available data are not sufficient to fully support the established tolerance for pendimethalin residues in or on sunflower seeds because the data pertaining to processed products of sunflower seed were not obtained from sunflower seeds bearing detectable weathered residues. However, additional data will not be required for sunflower seed processed products because identical data gaps exist for soybean processed products. Upon receipt of the requested soybean processing study (for particulars see p. 61), data pertaining to residues of pendimethalin in meal, hulls, and oil (crude and refined) of soybeans will be translated to sunflower seed. No Canadian or Mexican tolerance or Codex MRL exists for pendimethalin residues in or on sunflower seed.

Reference (used):

American Cyanamid Co. 1980. Residue Report Nos. C-985, C-982, C-1639, C-1722 to C-1730 in Section D of PP#0F2373(242640).

Discussion of the data:

American Cyanamid Co. [PP# 0F2373 (242640)] submitted data pertaining to combined residues of pendimethalin per se and its metabolite (CL 202,347) in or on sunflower seeds and foliage from tests (the number of tests per state is given parenthetically) conducted in CA (2), MN (9), ND (3), SD (10), and TX (2). Combined residues were nondetectable (<0.1 ppm, including pendimethalin per se and CL 202,347 each at <0.05 ppm) in or on 20 sunflower seed samples harvested 125-150 days following a single preplant incorporated application (made with ground or aerial equipment) with the 4 lb/gal EC formulation at 0.5-1.5 lb ai/A (1x the maximum registered rate) either alone, tank-mixed, or followed by a preemergence application with chloramben. Eleven plant samples (foliage) harvested from similar tests also yielded nondetectable (<0.1 ppm) combined residues. Additional tests reflected preplant use of the 4 lb/gal EC formulation at exaggerated rates of 3-4 lb ai/A (2-2.7x) and postemergence use at 1.25-3 lb ai/A alone or tank-mixed with chloramben. Combined residues were nondetectable (<0.1 ppm) in or on six seed samples harvested 144-160 days following one of the above treatments.

Processed commodities were generated from sunflower seeds, which received field treatments at 1.25-1.5 lb ai/A (Report Nos. C-1723, C-1730, and C-1726), and bore nondetectable combined residues (<0.1 ppm, including pendimethalin per se and CL 202,347 each at <0.05 ppm). Combined residues (three samples each) were nondetectable (<0.1 ppm) in oil, meal, hulls and soapstock.

Adequate electron capture GC methods were used for quantification of pendimethalin per se and CL 202,347 in sunflower seed and meal (M-701 and M-702), sunflower plants (M-702 and M-706-AFID), and sunflower oil (M-704 and M-708). The test states of MN, ND, and TX provide adequate geographic representation since these states produce virtually all of the U.S.-grown sunflowers (Agricultural Statistics, 1982, p. 135). In our opinion the data provide inadequate support for the established sunflower seed tolerance because the processing studies did not utilize samples bearing measurable weathered residues of pendimethalin; therefore the available studies fail to indicate whether or not residues will concentrate upon processing. Based upon the fact that sun-

flower oil is readily extractable into hexane, we feel that additional data are warranted. We conclude that the 0.1 ppm tolerance for pendimethalin residues in or on sunflower seed is numerically adequate but additional data reflecting residues in processed products (meal, hulls, soapstock, crude oil, and refined oil) may be required. The request for soybean processed products depend upon the results of additional requested metabolism studies. For particulars see p. 61.

Tobacco

Tolerance:

N/A (nonfood use).

Use directions and limitations:

The 4 lb/gal EC formulation has been registered for use on transplanted tobacco at 0.75-1.5 lb ai/A (exact rate is dependent upon soil texture) as a preplant incorporated application (broadcast or band) made using ground equipment; use in the states of FL, GA, MD, NC, SC, and VA may not exceed 1.25 lb ai/A. Application may be made immediately before or up to 60 days prior to transplanting and incorporation is to be made within 7 days after treatment (before transplanting). A number of state label registrations have been issued under Section 24(c) for this same formulation and use in GA (GA-790006), KY (KY-800002), MD (MD-800011), and PA (PA-800011). The 4 lb/gal EC has also been registered for use on tobacco as a direct spray application made after the last cultivation (layby; usually 4-6 weeks after transplanting) at 0.5-1 lb ai/A using ground equipment; application is made in a 16- to 24-inch band between the crop rows and in the row middles not contacting the tobacco plants.

The 3 lb/gal EC formulation (EPA Reg. No. 241-247) has been registered for sucker control in flue-cured tobacco at 1.5 lb ai/A and in burley tobacco at 1.9 lb ai/A using ground equipment. For flue-cured tobacco, two applications are used; the first made at early (first) flowering and the second made when

axillary buds are no greater than 1/2 inch long. For burley tobacco, only one application may be made per year applied immediately after topping when the majority of tobacco plants are in the early flowering stage. The 3 lb/-gal EC is formulated with xylene.

Conclusions:

The available data are not sufficient to assess the exposure of man to pendimethalin residues in or on tobacco. The following additional data are required:

- Residue data involving the metabolism of pendimethalin in tobacco using radioisotopic techniques. Data must include: the characterization and quantitation of metabolites found in or on the plant, determination if metabolites are translocated from soil, and characterization of photodegradation products.

- Residue data involving pendimethalin residues (including pendimethalin's 3,5-dinitrobenzyl alcohol metabolite if identified in the required plant metabolism study) in or on green freshly-harvested tobacco as the result of two treatments with the 3 lb/gal EC formulation at 1.5 lb ai/A. If residues exceed 0.1 ppm, additional data on pyrolysis products must be submitted.

References (used):

American Cyanamid Co. 1983. PROWL® herbicide EPA Reg. No. 241-243. Registration application for PROWL layby applications in tobacco. Report Nos. C-2202 and C-2203. Accession No. 250807. (No MRID assigned).

Discussion of the data:

Residue data were submitted by American Cyanamid Co. (Accession No. 250807) from 4 tests conducted in NC involving levels of pendimethalin per se in or on cured tobacco. Levels were <0.10 ppm (nondetectable) in or on four samples of cured tobacco 91-95 days after the second of two applications (using ground equipment) of the 4 lb/gal EC at 0.5-0.75 lb ai/A; the first application was a preplant incorporated treatment and the second was a directed layby treatment to the row middle. An adequate GC method (American Cyanamid Method No. M-550 which is similar to No. M-516 used for cotton foliage) was used for data collection. Data are not available involving the metabolism of pendimethalin in or on tobacco as a result of treatment with labeled pendimethalin; these data are required.

The available data do not adequately assess the exposure of man to the residues in or on tobacco because analyses were not performed for the metabolites of pendimethalin, green freshly-harvested tobacco samples were not used for determining residue levels, and the maximum registered rate was not used. We therefore conclude that additional data are required addressing the above mentioned inadequacies. Should residue levels in the required data exceed 0.1 ppm, further data submission will be necessary characterizing the pyrolysis products derived from pendimethalin.

MAGNITUDE OF THE RESIDUE IN MEAT, MILK, POULTRY, AND EGGS

Tolerances:

No tolerance has been established nor is any tolerance pending covering residues of pendimethalin in meat, milk, poultry or eggs.

Conclusions:

No direct animal treatments with pendimethalin formulations are registered. The maximum expected dietary intake of pendimethalin *per se* by food animals (beef and dairy cattle, poultry, and swine) is ~0.1 ppm if the diet consisted entirely of pendimethalin-treated feed items such as field corn grain, field corn forage or fodder, cottonseed, peanut meal and hulls, peanut vines or hay, rice grain, soybean meal, or soybean forage in any combination. Tolerances for pendimethalin residues in or on all of the above feed items are 0.1 ppm except in the cases of rice grain (0.05 ppm) and peanut hulls (0.25 ppm). Note that the establishment of the 0.1 ppm pending tolerances for sweet corn, beans (dry, lima, and snap), peas (dried and succulent), barley, wheat, safflower and sugarcane will not alter the maximum expected daily intake level of pendimethalin *per se* by food animals.

The metabolism of pendimethalin in ruminants (including milk) is not adequately understood because the [^{14}C]pendimethalin residues detected in goat tissues and milk (see Nature of the Residue in Animals section) were not identified. Since the residues of concern in animal products have not been delineated, at the present time we require data reflecting residues of pendimethalin *per se* and its metabolite CL 202,347. Other residues may need to be sought if requested metabolism studies so indicate. The following data are required:

- Lactating ruminants must be dosed with 0.1, 0.3, and 1.0 ppm pendimethalin *per se* (≥three animals/dose group) in the total diet until residues plateau in milk or for 28 consecutive days if no residues are detected in milk. Milk samples must be obtained twice daily. Animals must be sacrificed within

24 hours of the final dose and residues in tissues (muscle, liver, kidney and fat) determined.

If the additional requested plant metabolism studies indicate the presence of other detectable metabolites of concern, then metabolism studies for poultry may be needed. The need for a poultry feeding study will depend upon the results of the metabolism study for poultry.

The available goat metabolism study (see Nature of the Residue in Animals) indicates that residues of pendimethalin may occur in meat and meat by-products of food animals. Tolerances must be proposed for these food commodities, if the above-required data so indicate.

There are no Codex MRL or Mexican or Canadian tolerances for pendimethalin residues in animal products; therefore, no compatibility questions exist at the present time.

Reference (used):

Tondreau, R.E. 1973. PROWL (CL 92,553): Determination of CL 92,553 [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] Residues in Milk: Report No. C-384. (Unpublished study received Aug. 25, 1980 under 241-243; submitted by American Cyanamid Co. (CDL:099565-H; MRID No. 00067290).

Discussion of the data:

Tondreau (1973; MRID 00067290, CDL:099565-H) conducted a study in which three dairy cattle (unspecified variety) received unlabeled pendimethalin via gelatin capsules at a daily rate of 0.025 mg/kg body weight for 21 days; three additional animals served as controls. Residues of pendimethalin per se were nondetectable (<0.01 ppm) in nine milk samples from the 7-, 10-, and 21-day collection intervals. Residue quantitation was accomplished using an adequate

electron capture GC method (M-461; MRID 00023796). Presently, the residues of concern in animal products have not been delineated; therefore, feeding studies which indicate levels of pendimethalin per se and at least its metabolite CL 202,347 in animal products and by-products are required. The requested animal metabolism data may reveal other residues of concern.

MAGNITUDE OF THE RESIDUE IN FISH

Tolerance:

No tolerance presently exists for pendimethalin residues in fish.

Use directions and limitations:

The 4 lb/gal EC formulation of pendimethalin is registered for postemergence use on dry-seeded rice once per year at 0.75-1 lb ai/A; fresh water food fish may be exposed to pendimethalin if they are cultivated in pendimethalin-treated rice fields. When this type of aquaculture is practiced, catfish and crayfish are commonly introduced into rice fields 1-3 weeks after the permanent flooding which occurs between 5 to 7 weeks after rice is dry-seeded (personal communication with Dr. Brunson, Louisiana State University, Rice Experiment Station, telephone: 318-783-4373). Catfish are harvested 2-3 months after they are stocked (just prior to rice harvest). Rice fields containing crayfish are drained prior to rice harvest (the crayfish burrow into the mud) and are reflooded; crayfish reemerge from the mud and feed on the rice stubble until they are harvested in mid to late winter. There are presently no label restrictions pertaining to the use of pendimethalin on rice fields which are also used for aquaculture of freshwater food fish.

Conclusions:

The available data are not adequate to determine whether a tolerance covering pendimethalin residues in fish is necessary. The available fish metabolism studies yielded data which indicate that pendimethalin residues readily transfer to edible fish tissues, although residues did not tend to accumulate in substantial amounts in crayfish tissues. Since these data are not representative of the transfer and accumulation patterns which may occur in fish exposed to pendimethalin under field conditions, we feel that additional data reflecting this use are necessary. Alternatively, the registrant may propose label restrictions against the use of pendimethalin formulations on rice fields which are also used for aquaculture of fresh water food fish or crustaceans. The following data are required:

- Residues of pendimethalin *per se* and its metabolite (CL 202,347) in edible tissues of catfish and crayfish obtained from the following cultural conditions must be determined. A single postemergence application with the 4 lb/gal EC formulation at 1 lb ai/A should be made on established rice seedlings just prior to the permanent flood; catfish and crayfish should be introduced to the field 1 week after the permanent flood. Catfish samples must be obtained just prior to normal rice harvest; crayfish samples should be harvested in December of the same season. Tests should be conducted in AR (12%) and MS (69%); percent of food size catfish sales (The Aquaculture Outlook and Situation, April, 1981, p. 16) given parenthetically.

There are no Mexican or Canadian tolerances or a Codex MRL for pendimethalin residues in fish.

References (used):

Analytical Bio Chemistry Laboratories, Inc. 1980. Residue accumulation study in crayfish (*Procambarus simulans*) with ^{14}C-CL 92,553 (pendimethalin) under static conditions. Prepared for and submitted by American Cyanamid Co. under PP# OF2401 (099889). (No MRID assigned).

Kapoor, I.P. 1974. PROWL® herbicide: Metabolism X. Isolation, identification, and characterization of CL 92,553 and its metabolites in fish and its aquatic environment. Exhibit 43, Section H. Submitted by American Cyanamid Co. under PP# 5G1567. (Unknown accession number; no MRID assigned).

Discussion of the data:

No data are available pertaining to pendimethalin residues in edible tissues of catfish or crayfish grown in pendimethalin-treated rice fields. Studies pertaining to the metabolism of pendimethalin in catfish (Kapoor, 1974) and crayfish (Analytical Bio Chemistry Laboratories, Inc., 1980) are available

and the salient data from these reports are presented here in brief; for a detailed discussion of these data, refer to the Magnitude of the Residue in Animals section. Both of the above-referenced studies utilized static, laboratory-simulated aquatic systems which contained soil treated with 14C ring-labeled pendimethalin at 1-2 lb ai/A. Residues of [^{14}C]pendimethalin equivalents reached maximum levels in edible catfish and crayfish tissues after 14 and 7 days of exposure, respectively; residues in both catfish and crayfish tissues declined during the remaining treatment periods. Conversely, total 14C residues in water samples obtained from these simulated systems increased from 0.004 ppm to 0.014 ppm (1- to 42-day catfish study) and from 0.014 to 0.032 ppm (1- to 14-day crayfish study). It is noteworthy that data pertaining to residues of pendimethalin in water from pendimethalin-treated rice fields (refer to Magnitude of the Residue in Potable Water section) indicated a decline in residues from 0.057 ppm at 8 days posttreatment to nondetectable levels (<0.002 ppm) at 42 days posttreatment.

We feel the available data from the fish metabolism studies conducted in a simulated aquatic system are not adequate to render an opinion regarding the necessity (or lack of necessity) of a tolerance for fish. Therefore, we require additional data depicting pendimethalin residues in fish cultured in pendimethalin-treated rice fields. Adequate analytical methods are available for the quantitation of pendimethalin per se in fish tissues [Report No. C-795, Method No. M-632 (MRID 00058835)]; however, a validated method for the quantitation of CL 202,347 must be submitted. As an alternative to the requested field trial, the registrant may propose a label restriction prohibiting the use of pendimethalin on rice fields also used for the production of food fish.

REGULATORY INCIDENTS

The Food and Drug Administration sent us a report (July 13, 1984, Ellis Gunderson) by which they notify us that during the years 1978 to present no residues of pendimethalin have been detected in either domestic or imported foods sampled or in Total Diet Studies. Pendimethalin is determined by multi-residue methodology (PAM I, 212.2/232.4) which is used in analyzing a large number of non-fatty raw agricultural commodities. During the above mentioned time period over 25000 samples were analyzed by this methodology.

TOLERANCE REASSESSMENT SUMMARY

Sufficient data are available to determine that the established tolerance for combined residues of pendimethalin and its 3,5-dinitrobenzyl alcohol metabolite (CL 202,347) in or on the following commodities are adequate: corn forage and fodder, peanut forage, hay and hulls, potatoes, sorghum grain, and sorghum forage and fodder [40 CFR 180.361 (a) and (b)]. Additional data are required to support the tolerances for pendimethalin residues in or on soybean forage and hay. Data gaps also exist for the processed products of corn, cottonseed, peanuts, soybeans, and sunflower seeds Additional metabolism are requested. Depending on the results of these data, additional processing studies for soybeans may be required. If requested this processing study will be translated to corn, cottonseed, peanuts, and sunflowers seeds. No additional data are required for rice grain; however, we recommend that the rice tolerance be increased from 0.05 ppm to 0.1 ppm. Data gaps exist for tobacco and fish raised in rice fields. We do not recommend the establishment of any crop group tolerances at this time. Prior to the submission of the requested animal and plant residue studies, it is imperative that the data gaps be satisfied for animal and plant metabolism, and storage stability. Refer to the preceding sections for details of data gaps.

The ADI for pendimethalin is 0.0125 mg/kg/day. The TMRC (as of 2/29/84) is 0.0113 mg/day based on a 1.5-kg diet. Note that peanuts, rice, and sunflower seeds contribute an additional 0.001 mg/day to the TMRC. Tolerances pending for the following commodities would affect the TMRC: barley, beans, peas, safflower, sugarcane, sweet corn, tomatoes, and wheat.