UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

Date: 12/MAR/2008

Subject: Dichlobenil. Use on Caneberry (Subgroup 13-07A), Bushberry (Subgroup 13-07B). Summary of Analytical Chemistry and Residue Data. PP#7E7230.

DP Number: 349398
PC Code: 027401
40 CFR 180.231

Decision Number: 380110
MRID Number: 45572201
Chemical Class: nitrile herbicide

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Executive Summary

Interregional Research Project No. 4 (IR-4) has requested tolerances for the use of dichlobenil (2,6-dichlorobenzonitrile) on rhubarb, caneberry, subgroup 13-07A, and bushberry, subgroup 13-07B commodities. Dichlobenil is a nitrile herbicide that acts by inhibiting germination of actively dividing meristems and acts primarily on growing points and root tips. The rhubarb request was previously reviewed by W. Cutchin (DP Num: 31566, 22/FEB/2006). Dichlobenil, formulated as the 4% granular product Casoron® 4G (EPA Reg. No. 400-168), is to be applied at a maximum seasonal rate of 4 lb ai/A to berry commodities. The product is applied directly to soil while the target crop is dormant. For berry crop group tolerances, no additional data was submitted. Tolerances are currently established for blackberry, blueberry, and raspberry. Since the previously reviewed data encompasses the representative commodities for the requested berry crop groups, the data may be translated to support the requested berry tolerances.

The qualitative nature of the residue in plants is adequately understood based on acceptable plant metabolism studies on apples and grapes. Both studies indicate that the major residue of concern is 2,6-dichlorobenzamide (BAM). The parent compound, dichlobenil, was not detected in either of the studies. HED concluded that BAM is the major terminal residue of dichlobenil in plants, and should be added to the tolerance expression. Since there are no berry animal feed items of regulatory concern, a discussion of the nature of the residues of dichlobenil in livestock commodities is not germane to this action.

Pesticide Analytical Manual (PAM) Vol. II, Method A is a gas-liquid chromatography/electroconductivity detector (GLC/ECD) method with a limit of detection (LOD) of 0.05 ppm, which can be used for determination of residues of dichlobenil in/on plant commodities. This method was judged adequate for tolerance enforcement. However, the registrant was required to revise the method or develop an alternative method using safer solvents. The revised method is not adequate and will require additional modification before it can be accepted as a tolerance enforcement method. A GLC/ECD method, L 3-53-71, for determination of residues of BAM in/on fruits and nuts has undergone a successful independent laboratory validation and has been validated by the EPA Analytical Chemistry Laboratory (ACL). However, a revised method incorporating ACL's comments must be submitted before the requirements for an analytical method for BAM can be considered fulfilled. Dichlobenil is completely recovered using the multiresidue methods in PAM Vol. I Sections 302 and 304. BAM is also completely recovered using Section 302. Since the multiresidue methods adequately quantitate dichlobenil and BAM, there is adequate enforcement methodology for this action.

The analytical methods SOP# Meth-83, *Determination of Dichlobenil Residues in Cherries* and SOP# Meth-84, *Determination of 2,6-dichlorobenzamide Residues in Cherries*, developed by Morse Laboratories were used with minor modifications for the analysis of dichlobenil residues on rhubarb. Dichlobenil residues were extracted from the raw agricultural commodity (RAC) by extracting with ethyl acetate/hexane and clean up using a Florisil column. BAM residues were extracted from RAC by extracting with ethyl acetate and clean up using a Florisil column. Samples were analyzed using a GLC/ECD in halogen mode. The analytical method was validated at 0.05, 0.1, and 0.5 ppm for dichlobenil and 0.01, 0.02, and 0.1 ppm for BAM. At the range of the fortification levels, method recoveries were generally within Agency standards of 70-120%. The lower limit of method validation (LLMV) was reported for dichlobenil and BAM as 0.05 ppm and 0.01 ppm, respectively. The LOD was 0.006 ppm for both dichlobenil and BAM. The method used for data collection is adequate

There are no processed commodities of regulatory interest resulting from the requested berry uses. Berry crops are not rotated on a regular basis; therefore, inadvertent residues in rotational crops are not a concern for this action.

Regulatory Recommendations and Residue Chemistry Deficiencies

Pending receipt of the revised Section F, revised Section B and the forthcoming human health risk assessment, ARIA previously recommended the tolerances of the combined residues of the

herbicide dichlobenil (2,6- dichlorobenzonitrile) and its metabolite 2,6-dichlorobenzamide in/on rhubarb at 0.06 ppm (DP Num: 315266, W. Cutchin, 22/FEB/2006) and recommends the following tolerances for the requested berry commodities at the levels listed below:

Caneberry, Subgroup 13-07A	0.10 ppm
Bushberry, Subgroup 13-07B	0.15 ppm

The revised Reregistration Eligibility Decision (RED) (K. Boyle, 31/JUL/1996) recommended deletion of a stone fruit crop group tolerance which was not being supported by the petitioner and establishment of a separate tolerance on cherries. However, as stated in the previous RED, the stone fruit crop group was included in this dietary exposure assessment since as long as the tolerance exists commodities containing BAM residues could be imported (Dichlobenil: The Revised HED Chapter of the RED, Case 0263, Chemical 027401, 027402 (BAM), K. Boyle, 31/JUL/1996,).

Background

Dichlobenil is a nitrile herbicide that acts by inhibiting germination of actively dividing meristems and acts primarily on growing points and root tips.

TABLE 1. Test Compound Nomenclature.

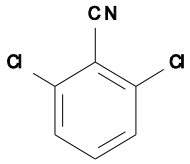
Compound	Chemical Structure
	
Common name	dichlobenil
Company experimental name	DCBN
IUPAC name	2,6-dichlorobenzonitrile
CAS name	2,6-dichlorobenzonitrile
CAS #	1194-65-6
End-use product/(EP)	Casoron® 4G (EPA Reg. No. 400-168)

TABLE 2. Physicochemical Properties of Dichlobenil.

Parameter	Value	Reference
Melting point/range	145°C	RED Chapter, 6/29/95
pH	NA	
Density	1.3 g/cm^3	IPS Inchem, 4/05
Water solubility (25°C)	0.0021g/100mL	RED Chapter, 6/29/95
Solvent solubility (g/100mL at 25°C)	xylene 5.3 ethanol 1.5 cyclohexane 0.37	
Vapor pressure at 20°C	5.5 x 10-4 mmHg	IPS Inchem, 4/05
Dissociation constant (pK_a)	NA	
Octanol/water partition coefficient Log(K_{OW})	2.64	IPS Inchem, 4/05
UV/visible absorption spectrum	NA	

860.1200 Directions for Use

TABLE 3. Summary of Directions for Use of Dichlobenil.

Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A)	PHI (days)	Use Directions and Limitations
Bushberry, Subgroup 13-07A (Blueberry, Currant, Elderberry, Gooseberry, Huckleberry, Aronia berry, Blueberry lowbush, Buffalo currant, Chilian guava, European barberry, Highbush cranberry, Honesuckle, Jostaberry, Juneberry, Lingonberry, Native currant, Salal, Sea buckthorn)						
Apply only to established plantings using granular applicator Maybe used on bearing, non-bearing, and nursery stock. Do not apply until 4 weeks after transplanting.	Casoron® 4G [400-168]	4 6	1 (assumed)	4 6	NA	Do not apply during new shoot emergence.
Caneberry, Subgroup 13-07B (Blackberry, Raspberry, Boysenberry, Dewberry, Loganberry, Wild Raspberry)						
Apply only to established plantings using granular applicator	Casoron® 4G [400-168]	4	1 (assumed)	4	NA	Do not apply during new shoot emergence. Do not allow livestock to graze on treated orchards.

* Highlighted areas represent wording of the Section B that differs from the proposed label.

Conclusions. The label is adequate to allow evaluation of the residue data relative to the proposed uses on caneberry, subgroup 13-07A. However, the Section B must be revised for the bushberry, subgroup 13-07B from 6 lbs ai/A to 4 lbs ai/A to match the label use and submitted data for the bushberry, subgroup 13-07B commodities. Also, the label and Section B must be revised to correctly spell the commodities containing "currant" in the name.

860.1300 Nature of the Residue - Plants

Dichlobenil RED, October 1998

The qualitative nature of the residue in plants is adequately understood based on acceptable plant metabolism studies on apples and grapes. Both studies indicate that the major residue of concern is BAM. The parent compound, dichlobenil, was not detected in either of the studies. On June 8,

1992, HED concluded that BAM is the major terminal residue of dichlobenil in plants, and should be added to the tolerance expression. Because dichlobenil plant metabolism studies demonstrate that 2,6-dichlorobenzoic acid (2,6-DCBA) is not a plant metabolite, HED has recommended removing 2,6-DCBA from the tolerance expression for dichlobenil. Therefore, residue data for 2,6-DCBA are no longer required. All conclusions specified here regarding the status of residue chemistry data requirements and the adequacy of the established tolerances reflect the determination to add BAM to the tolerance expression and remove 2,6-DCBA from the tolerance expression.

Conclusions. The residues of concern in plants are the parent dichlobenil and the metabolite BAM.

860.1300 Nature of the Residue - Livestock

Since there are no berry animal feed items of regulatory concern, a discussion of the nature of the residue of dichlobenil is not germane to this action.

860.1340 Residue Analytical Methods

Dichlobenil RED, 10/98
45572201.der.doc, W. Cutchin, 22/FEB/2006

PAM Vol. II, Method A is a GLC/ECD method with a detection limit of 0.05 ppm, which can be used for determination of residues of dichlobenil in/on plant commodities. This method was judged adequate for tolerance enforcement; however, Method A uses benzene as a solvent. The registrant was required to revise the method or develop an alternative method using safer solvents. This method will likely require additional modification before it can be accepted as a tolerance enforcement method. The Dichlobenil Guidance Document (23/MAR/1987), referenced in the RED document, required the development of an analytical method for the detection and quantitation of BAM in plant commodities. The former basic producer, Solvay Duphar, submitted a GLC/ECD method (L 3-53-71) for determination of residues of BAM in/on fruits and nuts. This method has undergone a successful independent laboratory validation and has been validated by the EPA Beltsville ACL. However, a revised method incorporating ACL's comments must be submitted before the requirements for an analytical method for BAM can be considered fulfilled.

The analytical methods SOP# Meth-83, *Determination of Dichlobenil Residues in Cherries* and SOP# Meth-84, *Determination of 2,6-dichlorobenzamide Residues in Cherries*, developed by Morse Laboratories were used with minor modifications for the analysis of dichlobenil residues on berry matrices. Dichlobenil residues were extracted from the RAC by homogenizing the samples with ethyl acetate/hexane and rotovaping the supernatant almost to dryness. The residue is then redissolved in hexane and cleaned up using a Florisil column. The dichlobenil residues are eluted with ethyl acetate/hexane, rotovaping the eluant almost to dryness, and the sample redissolved in hexane for analysis. BAM residues were extracted from the RAC by homogenizing the samples with ethyl acetate and taking the supernatant almost to dryness. The residue is then redissolved in hexane and cleaned up using a Florisil column. The BAM residues are eluted with ethyl acetate/hexane, taking the eluant almost to dryness, and the sample redissolved in hexane for analysis. A GLC/ECD in halogen mode was used for the analysis. The analytical method was

validated at 0.05, 0.1, and 0.5 ppm for dichlobenil and 0.01, 0.02, and 0.1 ppm for BAM. At these fortification levels, method recoveries were generally within Agency standards of 70-120%. The petitioner presented adequate sample chromatograms and calibration curves. The LLMV was reported for dichlobenil and BAM as 0.05 ppm and 0.01 ppm, respectively. The LOD was 0.006 ppm for both dichlobenil and BAM.

Conclusions. The previously submitted methods proposed for tolerance enforcement for dichlobenil and BAM on plants are not adequate for the reasons described above. However, as the multiresidue methods adequately quantitate dichlobenil and BAM (see, 860.1360, below), there is no deficiency for this action. The method used for data collection is adequate.

860.1360 Multiresidue Methods

Dichlobenil RED, October 1998

The FDA PESTDATA database dated 1/94 (PAM Vol I, Appendix I) indicates that dichlobenil is completely recovered (>80%) using multiresidue methods PAM Vol. I Sections 302 (Luke method) and 304 (Mills fatty food method), and has partial recovery (50-80%) using Section 303 (Mills, Onley, Gaither method). The database also indicates that BAM is completely recovered (>80%) using Section 302.

860.1380 Storage Stability

DP Num: 179079, C. Olinger, 09/FEB/1993
DP Num:182600, C. Olinger, 05/MAR/1993

Since the representative berry commodity samples were stored for less than 35 days at -18ºC between harvest and analysis, additional storage stability data is not required for these RACs.

860.1480 Meat, Milk, Poultry, and Eggs

Since there are no berry livestock feed items of regulatory concern, a discussion of dichlobenil residues in livestock commodities is not germane to this action.

860.1500 Crop Field Trials

DP Num: 179079, C. Olinger, 09/FEB/1993
DP Num:182600, C. Olinger, 05/MAR/1993

Caneberry, Subgroup 13-07A and Bushberry, Subgroup 13-07B

No additional field trial studies have been submitted. The petitioner has requested that current tolerances on blackberry, blueberry, and raspberry in combination with previously submitted studies be translated to include tolerances on caneberry, subgroup 13-07A, and bushberry, subgroup 13-07B.

Adequate data on blackberry, blueberry and raspberry is available to support the requested tolerances. **ARIA recommends for the establishment of tolerances for dichlobenil residues in/on caneberry, subgroup 13-07A at 0.10 ppm, and bushberry, subgroup 13-07B at 0.15 ppm. A revised Section F is required.**

860.1520 Processed Food and Feed

Since there are no berry processed food items of regulatory concern, a discussion of dichlobenil residues in processed commodities is not germane to this action.

860.1650 Submittal of Analytical Reference Standards

No analytical reference standards are available in the Agency's Pesticide Repository. However, both dichlobenil and BAM are available as reference standards in the commercial market place.

860.1850 & 860.1900 Confined and Field Accumulation in Rotational Crops

The requested berry commodities are perennial crops; therefore a discussion of residues in rotational crops is not germane to this action.

860.1550 Proposed Tolerances

Dichlobenil residues of concern are parent dichlobenil and the metabolite BAM (2,6-dichlorobenzamide) as stated in 40 CFR §180.231. There are no international harmonization issues associated with this action.

TABLE 5. Tolerance Summary for Dichlobenil

Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments (correct commodity definition)
Rhubarb*	0.15	0.06	
Caneberry, Subgroup 13A	0.1	0.10	Caneberry, Subgroup 13-07A
Wild raspberry	0.1	NA	Member of new Caneberry, Subgroup 13-07A.
Bushberry, Subgroup 13B	0.15	0.15	Bushberry, Subgroup 13-07B.
Aronia berry	0.15	NA	Member of new Bushberry, Subgroup 13-07B.
Blueberry, lowbush	0.15	NA	Member of new Bushberry, Subgroup 13-07B.
Buffalo currant	0.15	NA	
Chilian guava	0.15	NA	
European barberry	0.15	NA	
Highbush cranberry	0.15	NA	
Honeysuckle	0.15	NA	
Jostaberry	0.15	NA	
Juneberry	0.15	NA	
Lingonberry	0.15	NA	
Native currant	0.15	NA	
Salal	0.15	NA	

Sea buckthorn	0.15	NA

* Recommended in DP Num: 315266, W. Cutchin, 22/FEB/2006.

INTERNATIONAL RESIDUE LIMIT STATUS

Chemical Name: 2,6-dichlorobenzonitrile	Common Name: Dichlobenil	√ Proposed tolerance Reevaluated tolerance Other	Date: 01/22/2008

Codex Status (Maximum Residue Limits)	**U. S. Tolerances**
√ No Codex proposal step 6 or above No Codex proposal step 6 or above for the crops requested	Petition Numbers: 2E6398, 7E7320 DP Num: 341453, 315266 Other Identifier:
Residue definition (step 8/CXL): N/A	Reviewer/Branch: D. Rate
	Proposed Residue definition: Combined residues of dichlobenil and metabolite 2,6-dichlorobenzamide (BAM)

Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
		Rhubarb	0.06
		Caneberry, Subgroup 13A	0.1
		Wild raspberry	0.1
		Bushberry, Subgroup 13B	0.15
		Aronia berry	0.15
		Buffalo currant	0.15
		Chilian guava	0.15
		European barberry	0.15
		Highbush cranberry	0.15
		Honeysuckle	0.15
		Jostaberry	0.15
		Juneberry	0.15
		Lingonberry	0.15
		Native currant	0.15
		Salal	0.15
		Sea buckthorn	0.15

Limits for Canada	**Limits for Mexico**
√ No Limits No Limits for the crops requested	√ No Limits No Limits for the crops requested
Residue definition: N/A	Residue definition: N/A

Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)

Notes/Special Instructions: S. Funk, 01/30/2008.