



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

FEB 22 1991

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#OE3889: Chlorothalonil (Daconil®, Bravo®) in or on Blueberries. Evaluation of Analytical Methods and Residue Data (MRID #416149-0 and -1 (two volumes); CBTS #7029)

FROM: W. T. Chin, Ph.D., Chemist *W. T. Chin*
Tolerance Petition Section III
Chemistry Branch Tolerance Support I
Health Effects Division (H7509C)

THRU: P. V. Errico, Section Head *P. V. Errico*
Tolerance Petition Section III
Chemistry Branch Tolerance Support I
Health Effects Division (H7509C)

TO: Joanne Miller, PM #21
Fungicide-Herbicide Branch
Registration Division (H7505C)

and

Toxicology Branch
Health Effects Division (H7509C)

The Petitioner, IR-4, on behalf of the Agricultural Experiment Stations of North Carolina, Oklahoma, Texas, Florida, Louisiana, Georgia, South Carolina, Tennessee, Michigan, Kentucky, Pennsylvania and Washington requests the establishment of a tolerance for the residues of the fungicide chlorothalonil, 2,4,5,6-tetrachlorophthalonitrile (SDS-2787) and its metabolite, 4-hydroxy-2,5,6-trichlorophthalonitrile (SDS-3701) in or on the raw agricultural commodity blueberry at 1.0 ppm. A letter of authorization written by R. P. Burton of Fermenta ASC Corporation dated 5/18/90 is submitted.

Tolerances are established for residues of chlorothalonil and its

metabolite SDS-3701 in/on various raw agricultural commodities ranging from 0.05 to 15 ppm under 40 CFR 180.275.

A registration standard for chlorothalonil has been issued (9/30/84, Acc #258778).

CONCLUSIONS

1. The nature of chlorothalonil in blueberries is adequately understood. The parent compound and its metabolite SDS-3701 are of regulatory concern.
2. The petitioner is requested to revise Section B modifying the sentence "Do not apply after full bloom (early petal fall) or within 42 days of harvest" to "Do not apply after full bloom (early petal fall) or within 42 days before harvest."
3. There are no feed items associated with the proposed use on blueberries. Therefore, there should be no problems with secondary residues in meat, poultry, milk and eggs.
4. Adequate enforcement methods are available in PAM II for residues of chlorothalonil and SDS-3701. The Protocol I of the FDA multiresidue methods is adequate to determine the HCB and PCBN impurities present in technical chlorothalonil.
- 5a. The residue data generated from the proposed formulation BRAVO® 720 are considered adequate to support the proposed 1.0 ppm tolerance of chlorothalonil and its metabolite SDS-3701 in/on blueberries.
- 5b. Since no residue data were submitted from the formulation BRAVO®90DG, the petitioner is requested either to revise Section B deleting this formulation or to submit residue data generated from this formulation.
- 5c. None of the metabolites (SDS-3701 and SDS-46851) and the manufacturing impurities (HCB or PCBN) were detected on the treated blueberries at harvest.
6. No animal feed items are involved with this proposed use. Therefore, there are no concerns with respect to secondary residues in meat, milk, poultry and eggs.
7. There are no Canadian, Mexican and Codex tolerances for chlorothalonil and its metabolites established in/on blueberries. Therefore, there are no compatibility problems involved in this petition.

Metabolites
not
flowable

RECOMMENDATION

Pending the resolution of the deficiency identified in Conclusions

#2, #5b and TOX considerations permitting, DEB recommends for the establishment of a tolerance for the residues of chlorothalonil and its metabolite SDS-3701 in or on the raw agricultural commodity blueberry at 1.0 ppm.

DETAILED CONSIDERATIONS

Manufacture and Formulations

The manufacturing process of technical chlorothalonil and a discussion of its impurities, including HCB (hexachlorobenzene) and PCBN (pentachlorobenzonitrile), have been previously reported in detail in connection with PP#4E1502 (see R. Schmitt's 11/27/74 memo).

The proposed formulations of chlorothalonil are: BRAVO® 720 (EPA Reg. #50534-188), BRAVO® 500 (EPA Reg. #50534-8) and BRAVO® 90DG (EPA Reg. #50534-157). BRAVO® 720 and BRAVO® 500 formulations are liquid concentrates containing 6.0 lb ai/gal (54.0% ai and 46.0% inerts) and 4.17 lb ai/gal (40.4% ai and 59.6% inerts), respectively. BRAVO® 90DG is a water-dispersible granular formulation containing 90.0% ai and 10.0% inert.

Proposed Use

Supplemental labels submitted in section B are summarized below:

Disease	Formulation	Dosage *pts(ai lbs)/A	Days/ Interval	Maximum rates/ Acre/Season
Mummy berry	BRAVO®720	3 (2.25)	7	15 pts(11.3 lb ai)
Anthraco		4 (3.00)	10	15 pts
Mummy berry	BRAVO®500	4 1/4 (2.22)	7	22 pts(11.5 lb ai)
Anthraco		5 3/4 (3.00)	10	22 pts
Mummy berry	BRAVO®90DG	2 1/2 (2.25)	7	13 lbs(12.0 lb ai)
Anthraco		3 1/4 (3.00)	10	13 lbs

* lbs for BRAVO®90DG.

Use in sufficient water (20-150 gallon/A) to obtain adequate coverage. Begin applications at budbreak (green tip) and repeat applications through the bloom period at the intervals indicated above. Do not apply after full bloom (early petal fall) or within 42 days of harvest. If additional disease control is required prior to harvest, use alternative registered materials and practices

The petitioner is requested to revise Section B modifying the sentence "Do not apply after full bloom (early petal fall) or within 42 days of harvest" to "Do not apply after full bloom (early petal fall) or within 42 days before harvest."

Nature of Residue

The nature of chlorothalonil in plants is adequately understood. A detailed discussion on metabolism of chlorothalonil in plants was reported in connection with PP#7F3471 (see J. Stokes' 5/30/90 memo). The parent compound and its metabolite, SDS-3701 are of regulatory concern for the proposed use on blueberries. CBTS has previously concluded that the technical impurities HCB and PCBN and a water soluble metabolite (SDS-46851, 3-carboxy-2,5,6-trichlorobenzamide) could be present in infinitesimal amounts and should not be of regulatory concern.

There are no feed items associated with the proposed use on blueberries. Therefore, there should be no problems with secondary residues in meat, milk, poultry and eggs.

Analytical Methodology

The method entitled "General Analytical Procedure for the Determination of Residues of Chlorothalonil (SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on Selected Crops" was used for generating the residue data submitted in this petition. Breifly: Residues of the above-mentioned five compounds in blueberry samples were extracted with a mixture composed of 380 ml acetone and 20 ml 10N sulfuric acid and then selectively partitioned into an organic solvent. The residues of chlorothalonil, HCB and PCBN were separated by column chromatography before subsequent quantitation by GC equipped with an electron capture detector. The residues

of SDS-3701 was derivatized to its methyl ether and the residue of SDS-46851 was derivatized to its methyl ester. The derivatives were separated by column chromatography and determined by GC with an electron capture detector. The limits of detection of this procedure are as follows: 0.01 ppm for chlorothalonil and SDS-3701, 0.03 ppm for SDS-46851, 0.003 ppm for HCB and 0.005 ppm for PCBN. The recoveries of the five compounds of interest from the fortified samples ranged from 70% to 120%. Adequate examples of calculation and chromatograms are provided.

The Protocol I of the FDA multiresidue methods are adequate to determine the HCB and PCBN impurities present in chlorothalonil technical.

CBTS concludes that this method is adequate and appears to be better than the enforcement method published in PAM II (method I). This new method can be sent to FDA as a lettered method for inclusion in PAM II.

Storage Stability Study

A report entitled "Residues of SDS-2787, SDS-3701, SDS-46851, HCB and PCBN In Cherries from a Stability Study (Field Incurred) - 1988 - One Year Interim Report" (MRID #415832-1) was submitted. Results of this study indicated that SDS-2787, HCB and SDS-3701 are stable over the time period evaluated; residue levels of SDS-46851 are too low to be statistically evaluated; and that the residue of PCBN decreased 50% over the time period evaluated.

CBTS concludes that this storage stability study is adequate to support the current petition.

Residue Data

Field trials were conducted in 1988 in Maine, Georgia, Mississippi, North Carolina, New Jersey and Michigan. BRAVO® 720 Fungicide was applied one to five times to blueberries at various growth stages from bud to pink berry and harvested 42 to 101 days after the last application. Residue data are summarized in Table 1 on the next page.

Table 1. Chlorothalonil Residues* in Blueberries

Location	Dosage (pts/A)	No. of Applin.	PHI (days)	Residues Determined (ppm)	
				SDS-2787	SDS-3701
Orono, Maine	0	0	0	<0.010	<0.010
				<0.010	<0.010
	3	3	68	0.024	<0.010
				0.024	<0.010
Blair- ville, GA	0	0	0	<0.010	<0.010
				<0.010	<0.010
	8	1	101	0.012	<0.010
				0.011	<0.010
	3	3	80	0.017	<0.010
				0.017	<0.010
Poplar- ville, MISS	0	0	0	<0.010	<0.010
				<0.010	<0.010
	3	5	42	0.201	<0.010
				0.318	<0.010
Castle Hayne, NC	0	0	0	<0.010	<0.010
				<0.010	<0.010
	3	5	49	<0.010	<0.010
				<0.010	<0.010
Mays Landing, NJ	0	0	0	<0.010	<0.010
				<0.010	<0.010
	3	4	75	0.542	<0.010
				0.595	<0.010
Grand Junction, MI	0	0	0	0.012	<0.010
				0.011	<0.010
	3	2	62	0.093	<0.010
				0.084	<0.010
	4.25	2	62	0.093	<0.010
				0.100	<0.010

* In all the above samples analyzed, <0.03, <0.003 and <0.005 ppm of SDS-46851, HCB and PCBN, respectively, were determined.

CBTS concludes that the field trials using BRAVO®720 only are reflective of the proposed use of chlorothalonil on blueberries. The Maximum 0.542 ppm residues of chlorothalonil and its metabolite SDS-3701 at the PHI of 75 days are less than the proposed 1.0 ppm. Based on the limits of detection no other residues were detected in the treated blueberry samples. CBTS concludes that these data are adequate to support the proposed 1.0 ppm tolerance for chlorothalonil and SDS-3701 in/on blueberries.

The proposed formulation BRAVO®720 is considered similar to BRAVO®500, but may be different from BRAVO®90DG as far as residue chemistry is concerned. Since no residue data were submitted from the formulation BRAVO®90DG, the petitioner is requested either to revise Section B deleting this formulation or to submit residue data generated from this formulation.

Meat, Milk, Poultry and Eggs

There are no feed items associated with proposed blueberries. Therefore, there should be no problem with secondary residues in meat, milk, poultry and eggs.

Other Consideration

There are no Canadian, Mexican and Codex tolerances for chlorothalonil established in/on blueberries. Therefore, there are no compatibility problems involved in this petition.

Attachment: Codex sheet.

cc: Circu, RF, PP#0E3889, W.T.Chin, R.D.Schmitt, PIB/FOD,
DRES/SACB

RDI: P.V.Errico(2/20/91), R.Loranger(2/20/91)
H709C: CBTS: CM#2, RM812, 557-4352, W.T.Chin,wc(2/20/91)