



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

SEP 27 1993

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MEMORANDUM

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

SUBJECT: PP#2E04042. Chlorothalonil (Bravo® 500 and Bravo® 720
Agricultural Fungicide, EPA Reg. No. 50534-8 and 50534-188) in
or on Asparagus. Amendment of 7/6/93.
MRID No. 428400-01, -02; CBTS No. 12277;
DP Barcode: D193368.

FROM: William D. Wassell, Chemist *W.D. Wassell 9/23/93*
Tolerance Petition Section I
Chemistry Branch I - Tolerance Support
Health Effects Division (H7509C)

THROUGH: Robert S. Quick, Section Head *Robert S. Quick*
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Chemistry Branch I - Tolerance Support
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TO: Hoyt L. Jamerson, PM - 43
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Summary of Deficiencies Remaining to be Resolved:

- Revised directions for use.
- Submission of adequate storage stability data.

Background/Summary:

W.L. Biehn, Ph.D., Associate Coordinator, Interregional Research Project No. 4 (IR-4), State Agricultural Experiment Station, Rutgers University, New Brunswick, New Jersey on behalf of the IR-4 Project and the Agricultural Experiment Stations of Kentucky, North Carolina, Oklahoma, Virginia and Washington requests the establishment of a tolerance under 40 CFR §180.275 for the combined residues of the fungicide chlorothalonil, [tetrachloroisophthalonitrile] and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile (also referred to as SDS-3701 or the 4-hydroxy metabolite of chlorothalonil) in or on the raw agricultural commodity (RAC) asparagus at 0.10 ppm.

The current submission consists of two volumes of data, a revised Section B and a cover letter addressing deficiencies cited in our previous review (see our memo of 11/13/92, W.D. Wassell). One of the volumes (MRID No. 428400-01)



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is an amendment to a previously submitted study; the original study had an MRID No. of 420739-01. The other volume of data consists of additional Magnitude of Residue data for chlorothalonil in/on asparagus. The previously cited deficiencies are restated below followed by the petitioner's response and finally our comments.

Conclusions:

1. CBTS concludes the proposed directions for use must be modified to specify a 120-day preharvest interval for asparagus grown in the state of California.
2. Information concerning the length and conditions of storage for samples of the 1991 - '92 field trials were not included in the current submission and the petitioner is instructed to submit this information.
3. CBTS concludes adequate storage stability data for chlorothalonil, its 4-hydroxy metabolite and the impurity HCB does not exist in our files to support the magnitude of residue trials submitted in support of the proposed use of chlorothalonil in/on asparagus. The petitioner is instructed to submit data pertaining to the storage stability of residues of chlorothalonil, SDS-3701 and HCB in asparagus over a period of 5 years and 7 months for further consideration of the subject petition. Alternately, the petitioner could conduct 3 additional field trials to replace those summarized in Table 1 (see Deficiency 1, in the Detailed Considerations section of this review) and provide storage stability data for chlorothalonil, its 4-hydroxy metabolite and HCB, assuming that the storage interval for the 1991 - '92 field trials was 7 months or less and the additional field trial samples will have a relatively short sample storage interval. We suggest conducting these additional field trials in the States of California, Washington and New Jersey.
4. Pending submission of adequate storage stability data and revision of the proposed directions for use, CBTS concludes the proposed tolerance level of 0.10 ppm for residues of chlorothalonil and its 4-hydroxy metabolite in/on asparagus is adequate and residues of the impurity HCB should be less than 0.009 ppm.

Recommendations:

Because of our concerns regarding the storage stability of residues of chlorothalonil, its 4-hydroxy metabolite and the impurity HCB and the need for a revised Section B, CBTS recommends against the proposed tolerance for chlorothalonil and its 4-hydroxy metabolite in/on asparagus. For further consideration the petitioner is instructed to submit adequate storage stability data for chlorothalonil, its 4-hydroxy metabolite and the impurity HCB in/on asparagus as outlined in Conclusion 3, above. Alternatively, additional field trials and storage stability data are needed.

Detailed Considerations

Deficiency 1: CBTS concludes the proposed directions for use of the product on asparagus are not adequate. We request a revised Section B that includes a maximum seasonal use rate and a pre-harvest interval that reflects the residue data.

Petitioner's Response: The petitioner has submitted a revised Section B. The proposed directions for use of Bravo® 720 and Bravo® 500 (EPA Reg Nos. 50534-188 and 50534-8, respectively) on asparagus now include the following instructions: Applications are to begin after harvest of the spears at a rate of 1.5 to 3.0 lbs ai/A with repeat applications at 2 to 4 week intervals until the ferns are no longer productive. Do not apply more than a total of 9 lbs ai/A/season. A preharvest interval of 190 days is specified.

CBTS Comments: CBTS concludes the directions for use are adequate for all areas of the country except CA. Following discussions with Bob Mullen, Ph.D. of the University of CA at Davis, CA and Keith Mayberry, Ph.D. of the University of CA, at Imperial, CA, we have determined that a preharvest interval of 120 days would be more practical for northern areas of the state, but that a preharvest interval of 30 to 60 days is needed for the southern areas of the state. In the southern areas of the state, Dr. Mayberry indicated that a large portion of the asparagus growers cut the ferns in mid August and depending upon the irrigation schedule may begin harvest as little as 20 days later. However, as a result of the EBDCs Special Review, the Agency has concluded that a minimum preharvest interval of 120 days is required for a similar use of the EBDCs on asparagus grown in CA and AZ. In order to be consistent with the 120-day PHI accepted by the Agency for that use, a 120-day PHI will be needed for this chlorothalonil use in California.

Table 1 summarizes the field trials from the studies contained in MRID No. 420739-01 that were conducted in such a way as to closely match the proposed use pattern for chlorothalonil on asparagus. Also included in Table 1 are the sample storage lengths (see discussions concerning sample storage lengths below in association with Deficiency 3).

Table 1. Summary of Field Trial Data for Chlorothalonil in/on Asparagus which Most Closely Approximates the Proposed Use.

Location (Year)	No. of Applications (Formulation)	Application Rate (lbs ai/A)	Total Rate (lbs ai/A)	PHI (days)	Application Interval	Length of Storage
E. Lansing, MI (1987)	5 (Bravo® 720)	2.1	10.3	233	14 days	2 yrs. 6 months
	5 (Bravo® 500)	2.1	10.3	233	14 days	
Bixby, OK (1983)	8 (Bravo® 500)	1.6	12.5	215	10 - 15 days	5 yrs. 7 months
	8 (Bravo® 500)	3.1	25	215	10 - 15 days	
Stockton, CA (1987)	6 (Bravo® 720)	2.25	13.5	97	14 days	1 yr. 7 months
	3 (Bravo® 720)	3	9	107	28 days	

In addition to the field trials summarized in Table 1, the petitioner has submitted additional residue data reflecting the proposed use pattern. These field trials, which each consisted of two treated plots, were conducted in CA, WA, and MI during the 1991 - '92 growing season. The analytical portions of the studies were conducted at Hazelton Wisconsin, Inc. The analytical methodology was identical to that of the previously conducted studies and is outlined in our previous review of this petition (see our memo of 11/13/92, W.D. Wassell). Fortification recovery data for both the 1991 - '92 field trials and the previous field trials are included with our discussion concerning deficiency 3 below. Table 2 summarizes the 1991 - '92 field trials for chlorothalonil in/on asparagus (These studies are included in MRID No. 428400-02).

Table 2. Summary of Field Trial data for Chlorothalonil in/on Asparagus.

Location (Year)	No. of Applications (Formulation)	Application Rate (lbs ai/A)	Total Rate (lbs ai/A)	PHI (days)	Application Interval	Length of Storage
Roberts Island, CA (1991 - '92)	3 - ground (Bravo® 720)	3.0	9.0	189	38 to 49 days	unknown ¹
	3 - aerial (Bravo® 720)	3.0	9.0	195	38 to 49 days	
Moses Lake, WA (1991 - '92)	3 - aerial (Bravo® 720)	3.0	9.0	192	28 days	unknown
	6 - aerial (Bravo® 720)	1.5	9.0	192	14 days	

Location (Year)	No. of Applications (Formulation)	Application Rate (lbs ai/A)	Total Rate (lbs ai/A)	PHI (days)	Application Interval	Length of Storage
Conklin, MI (1991- '92)	3 - ground (Bravo® 720)	3.0	9.0	231	14 days	unknown
	6 - ground (Bravo® 720)	1.5	9.0	231	28 days	

¹ The storage interval for samples from each of the three field trials was approximately 7 months or less.

In all cases, four subsamples were taken from each plot. One subsample from the WA field trial exhibited chlorothalonil residues at 0.0326 ppm. In some cases, chlorothalonil residues below the method quantification limit of 0.03 ppm were detected. Residues above the quantification limits for the 4-hydroxy metabolite of chlorothalonil and HCB were not detected in any of the subsamples. The limit of quantification for HCB was 0.01 ppm and for the 4-hydroxy metabolite of chlorothalonil was 0.03 ppm.

CBTS concludes this deficiency is not resolved and the proposed directions for use must be modified to specify a 120-day preharvest interval for asparagus grown in CA. This shorter PHI for CA is supported by the 1987 Stockton, CA trials (see Table 1) in which a 97-day PHI was utilized in conjunction with an exaggerated rate (13.5 lbs ai/A, 1.5x) and a 107-day PHI was utilized in conjunction with the maximum proposed use rate (9.0 lbs ai/A).

Deficiency 2: The petitioner was instructed to revise the GLP Compliance statement contained in MRID No. 420739-01 as the statement pertained to only the analytical portion of the study and not the field portion of the study.

Petitioner's Response: The petitioner has submitted an amended report for the studies contained in MRID No. 420739-01. The amended report has been assigned the MRID No. 428400-01. The GLP Compliance Statement has been revised and now covers both the analytical and field portions of the studies.

CBTS Comments: This deficiency is resolved.

Deficiency 3: CBTS concluded the descriptions of the analytical procedures utilized in the submitted studies were not adequate and the petitioner was instructed to submit additional information concerning sample homogenization procedures, extraction procedures, analytical standards, instrument operating parameters, sample calculations, protocol deviations, complete sample histories and sample chromatograms.

Petitioner's Response: The petitioner has submitted an amendment to the original magnitude of residue report that includes the requested information.

CBTS Comments: This deficiency is not yet resolved. The petitioner has clarified the descriptions of the analytical procedures and has included the requested sample chromatograms. We are now able to determine the storage lengths for the samples of the studies included in MRID No. 420739-01. The storage lengths are included in Table 1 above. Information concerning the storage intervals for the samples of the studies included in 428400-02 were not given. However, based upon the dates of harvest and the study completion date, the storage length for all samples was 7 months or less. The petitioner is instructed to submit information concerning the storage length and conditions for the samples included in the 1991 - '92 field trials (MRID No. 428400).

The Residue Chemistry Chapter of the Chlorothalonil FRSTR (dated 2/16/88) indicates that additional data concerning the storage stability of residues of chlorothalonil, its 4-hydroxy metabolite and HCB are required for reregistration of the active ingredient. Data reviewed in conjunction with the Chlorothalonil FRSTR indicate that residues of chlorothalonil and SDS-3701 (the 4-hydroxy metabolite of chlorothalonil) are stable in passion fruit peel and pulp stored for a period of 6 months at -15°C and in mint hay stored for a period of 14 months at -20°C. Storage stability data for residues of HCB are not available. If our assumptions are correct concerning the storage interval for the 1991 - '92 field trials (i.e. 7 months or less), then there would be sufficient storage stability data for the residues of chlorothalonil and its 4-hydroxy metabolite to show there was no degradation of residue prior to analysis, but not for residues of HCB.

Several storage stability studies (MRID Nos. 428759-10 through -18) on various commodities have been submitted by ISK Biotech Corporation for review in reregistration. These studies are currently under review in CBRS. A storage stability study involving asparagus was not submitted. These studies were not extensively reviewed for the subject petition. The storage stability studies were conducted with field incurred residues on cucumber, carrots, celery, cherries, peanuts, potatoes, soybeans, tomatoes, and wheat grain. Samples were analyzed for residues of chlorothalonil, its 4-hydroxy metabolite, SDS-46851 (a soil metabolite), PCBN (a impurity of the technical product) and HCB. In several cases, the only detectable residue was the parent compound and in at least two cases all residues were below the method quantification limit. When detectable levels of HCB and the 4-hydroxy metabolite of chlorothalonil were present in the studies, the levels were either too low or highly variable or both, such that no conclusions on the storage stability of these compounds can be drawn from the submitted studies.

CBTS concludes adequate storage stability data for chlorothalonil, its 4-hydroxy metabolite and the impurity HCB does not exist in our files to support the magnitude of residue trials submitted in support of the proposed use of chlorothalonil in/on asparagus. The petitioner is instructed to submit data pertaining to the storage stability of residues of chlorothalonil, SDS-3701 and HCB in asparagus over a period of 5 years and 7 months for further consideration of the subject petition. Alternately, the petitioner could conduct 3 additional field trials to replace those summarized in Table 1 (above) and provide storage stability data for chlorothalonil, its 4-hydroxy

metabolite and HCB, assuming that the storage interval for the 1991 - '92 field trials was 7 months or less and the additional field trial samples will have a relatively short sample storage interval. We suggest conducting these additional field trials in the States of California, Washington and New Jersey.

A sufficient amount of information has now been submitted such that we can summarize the fortification recovery data for the studies. Table 3 contains a summary of fortification recovery data for the various field trials.

Table 3. A Summary of Fortification Recovery Data for Chlorothalonil, Its 4-hydroxy Metabolite and the Impurity HCB.

MRID No.	Statistical Element	Chlorothalonil	SDS-3701	HCB
420739-01	Fort. Range (ppm): Recovery Range: Average Recovery: Number of Forts.: σ_{n-1} :	0.03 to 5.0 70.5 to 134% 104% 15 17.2%	0.03 to 0.5 52.0 to 99.5% 78.3% 15 13.1%	0.01 to 0.05 72.7 to 106% 84.8% 15 10.7%
428400-02	Fort. Range (ppm): Recovery Range: Average Recovery: Number of Forts.: σ_{n-1} :	0.03 to 2.0 89.3 to 112% 102% 9 7.41%	0.03 to 0.4 70.0 to 118% 84.8% 9 18.7%	0.0091 to 0.03 68.0 to 84.8% 76.3% 9 5.56%

The petitioner has claimed quantification limits of 0.01 ppm for residues of chlorothalonil and its 4-hydroxy metabolite and 0.003 ppm for residues of HCB. Based upon the presented fortification recovery data, the demonstrated limit of quantification (LOQ) for chlorothalonil and its metabolite SDS-3701 is 0.03 ppm and for HCB the LOQ is 0.009 ppm.

Pending submission of adequate storage stability data and revision of the proposed directions for use, CBTS concludes the proposed tolerance level of 0.10 ppm for residues of chlorothalonil and its 4-hydroxy metabolite is adequate and residues of the impurity HCB should be less than 0.009 ppm.

cc: WDWassell, RF, Circ., PP#2E4042.
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