Shaughnessy No.: 081901

Date Out of EFGWB: 3/5/91

Copy of Review hand delivered to Ralph Burton 3/91

To: Lewis/Stone
Product Manager 21
Registration Division (H7505C)

From: Akiva Abramovitch, Section Head
Environmental Chemistry Review Section #3
Environmental Fate and Ground Water Branch/EFED (H7507C)

Through: Henry Jacoby, Chief
Environmental Fate and Ground Water Branch/EFED (H7507C)

Henry Jacoby

Attached, please find the EFGWB review of . . .

Reg./File # : 50534-8, -23, -157, -188, -189

Chemical Name : Chlorothalonil

Type Product : Fungicide

Product Name : Bravo

Company Name : Fermenta ASC Corporation

Purpose : Addendum to the chlorothalonil registration standard
Request to delete rotational crop restriction

Date Received: ____________ EFGWB # (s): 90-0748 to -0752

Deferrals to:
______ Ecological Effects Branch, EFED
______ Science Integration and Policy Staff, EFED
______ Non-Dietary Exposure Branch, HED
______ Dietary Exposure Branch, HED
______ Toxicology Branch I, HED
______ Toxicology Branch II, HED

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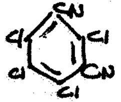
1. CHEMICAL:

Common name: Chlorothalonil.

Chemical name: 2,4,5,6-Tetrachloro-1,3-benzenedicarbonitrile.

Trade name(s): Bravo, Clortosip, Daconil 2787, Exotherm Termil.

Structure:



Formulations: 5% D, 2.5-11.25% G, 26.5-75% WP, 55 WP/D, 20% Impr, 90% DF, 3.75-6% EC, and 4.5-54% FlC.

Physical/Chemical properties:

Molecular formula: $C_8C_{14}N_2$.
Molecular weight: 265.89.
Physical state: Odorless, white crystalline solid.
Solubility: 0.6 ppm in water at room temperature; soluble in organic solvents at 25 C (w/w): xylene 8%, cyclohexane 3%, acetone 2%, and kerosene 1%.
Melting point: 245-247 C.
Vapor pressure: <0.01 mm Hg at 40 C.
Boiling point: 350 C at 760 mm Hg.
Stability: Stable to UV light; thermally stable under normal storage conditions.
Corrosivity: Noncorrosive.

2. TEST MATERIAL:

See individual studies.

3. STUDY/ACTION TYPE:

Addendum to the chlorothalonil registration standard; request to delete rotational crop restriction.

4. STUDY IDENTIFICATION:

Formanik, J.B. 1989. Field-soil dissipation of residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), its soil metabolites, and manufacturing impurities in soil from Bravo-treated areas - Fresno, CA. 1986-1988. Doc. No. 1401-86-0084-CR-003. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-29)

Kenyon, R.G. and D.L. Ballee. 1990. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated leafy crops from Bravo-treated areas - 1985-1987. Addendum I - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-010-001. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH. (MRID# 415648-39)

Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1989a. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated leafy crops from Bravo-treated areas -1985-1987. Doc. No. 1401-86-0084-CR-010. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-38)

Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1989b. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated leafy crops from Bravo-treated areas -1985-1987. Doc. No. 1401-86-0084-CR-010-002. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-40)

Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1990a. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in soybeans from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0097-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-23)

Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1990b. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in tomatoes from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0083-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-24)

Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1990c. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in wheat grain from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0070-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-27)

King, C. 1989. Field-soil dissipation of residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), its degradation products, and manufacturing impurities in soil from Bravo-treated areas - Greenfield, CA. 1986-1988. Doc. No. 1401-86-0084-CR-004. performed by Ricerca Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-30)

King, C., P.M. Prince, and D.L. Ballee. 1989a. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated oil bearing/bean crops from Bravo-treated areas - 1986, 1987. Doc. No. 1401-86-0084-CR-005. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-34)

King, C., P.M. Prince, and D.L. Ballee. 1989b. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated oil bearing/bean crops from Bravo-treated areas - 1986, 1987. Addendum I - peanut hay, bean hay, and pea fodder. Doc. No. 1401-86-0084-CR-005-001. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-35)

King, C., P.M. Prince, and D.L. Ballee. 1989c. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated oil bearing/bean crops from Bravo-treated areas - 1986, 1987. Report Amendment Number Three. Doc. No. 1401-86-0084-CR-005-003. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-37)

King, C., P.M. Prince, and D.L. Ballee. 1990d. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated oil bearing/bean crops from Bravo-treated areas - 1986,

1987. Addendum II - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-005-002. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-36)

King, C., J.L. Wiedmann, and D.L. Ballee. 1990e. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in celery from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0136-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-22)

King, C., J.L. Wiedmann, and D.L. Ballee. 1990f. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in cherries from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0068-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-26)

Rose, C.A., and D.L. Ballee. 1988. Determination of residues (field-soil dissipation) of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), its soil metabolites, and manufacturing impurities in soil from Bravo-treated areas - Donalsonville, GA. 1986-1988. Doc. No. 1401-86-0084-CR-002. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-28)

Rose, C.A. and D.L. Ballee. 1989a. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated root and bulb crops from Bravo-treated areas - 1987. Doc. No. 1401-86-0084-CR-009. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-32)

Rose, C.A. and D.L. Ballee. 1989b. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated grain crops from Bravo-treated areas - 1987. Doc. No. 1401-86-0084-CR-006. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-43)

Rose, C.A. and D.L. Ballee. 1989c. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated grain crops from Bravo-treated areas - 1987. Addendum I - straw and forage. Doc. No. 1401-86-0084-CR-006-001. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-44)

Rose, C.A. and D.L. Ballee. 1989d. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated grain crops from Bravo-treated areas - 1987. Report amendment. Doc. No. 1401-86-0084-CR-006-002. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-45)

Rose, C.A. and D.L. Ballee. 1990a. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated grain crops from Bravo-treated areas - 1987. Addendum II - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-006-003. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-46)

Rose, C.A. and D.L. Ballee. 1990b. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated root and bulb crops from Bravo-treated areas - 1987. Addendum I - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-009-001. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-33)

Rose, C., K.A. Dillon, and D.L. Ballee. 1990a. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in carrots from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0096-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-20)

Rose, C., K.A. Dillon, and D.L. Ballee. 1990b. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in potatoes from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0095-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-21)

Wiedmann J.L. and D.L. Ballee. 1990a. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated fruiting vegetables and cucurbits from Bravo-treated areas - 1985-1987. Doc. No. 1401-86-0084-CR-011. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-41)

Wiedmann J.L. and D.L. Ballee. 1990b. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on rotated fruiting vegetables and cucurbits from Bravo-treated areas - 1986-1987. Addendum I - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-011-001. performed by Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-42)

Wiedmann, J.L. and D.L. Ballee. 1990c. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in cucumbers from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0093-CR-001. performed by Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; submitted by Fermenta ASC Corp., Mentor, OH. (MRID# 415648-25)

5. <u>REVIEWED BY</u>:

B. Conerly
EFGWB/EFED/OPP
Review Section #3

Signature: E. B. Conerly, Chemist

Date: 2/25/91

6. <u>APPROVED BY</u>:

Akiva Abramovitch
EFGWB/EFED/OPP
Review Section #3

Signature: Akiva Abramovitch, Section Head

Date: FEB 25 1991

7. CONCLUSIONS:

Field Dissipation - Terrestrial -- These studies cannot be used to fulfill data requirements. Because the deficiencies cannot be resolved with submission of additional data, new studies are required.

Fresno, CA -- MRID# 415648-29. This study is unacceptable for several reasons listed below. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of chlorothalonil and its degradates. Plot 1 was later re-treated for the purpose of obtaining rotational crop accumulation data which is discussed separately (DER 4 of this document).

1) **These data do not serve to define a pattern or time course for the dissipation of chlorothalonil under field conditions.** The data appear to scatter, rather than vary in a regular fashion. Possible factors [*acknowledged by the study author*] which may have contributed to the irregularity of the data include atypical cultural practices, problems with the soil sampling technique, and the lack of irrigation and rainfall during the later sampling intervals. Most "movement" of chlorothalonil residues was attributed to cultivation and tillage prior to planting of the rotational crops or to contamination from upper soil layers during soil sampling. Parent compound was detected to the 12- to 15-inch depth, the deepest layer sampled. One degradate, 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701), was detected in all soil layers; no other degradates were detected (except for one isolated detection of 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851) in the upper 3 inches of one plot). Hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN), reported to be manufacturing impurities of the test substance, were detected to depths of 15 and 6 inches, respectively.

2) **Soil sampling may not have gone deep enough to define the extent of leaching of chlorothalonil and its degradates.** Chlorothalonil was detected at 0.01 ppm (average) in the lowest sampled depth (12 to 15" at 120 days following the last application made in 1986 at Plot 1, and at 318 days following the last application at Plot 2). In addition, soil was not sampled at 12-to 15-inch depth until 30 days posttreatment; it is possible that chlorothalonil may have been present in both plots at this depth prior to 30 days posttreatment. The soil should have been sampled at all sampling intervals to depths (preferably two sampling depths) at which residues were nondetectable.

3) Analyses were done on composited samples (and sampling variation thereby minimized). Without individual values for analyses, EFGWB cannot assess the "inherent" precision and accuracy of the procedures. For this reason, **EFGWB strongly**

recommends at least three independent samples for each sampling event.

4) The study author reported a half-life of 58 days for chlorothalonil in the upper 12 inches of soil using ***selected*** data from both treated plots. Because the residue levels were unusually high at certain sampling intervals (plot 1 at 0-30 days; plot 2 at 177 days and beyond), these data were not used in calculating the half-life. Since these values were arbitrarily discarded, the calculated half-life is considered to be of questionable validity.

Donalsonville, GA -- MRID# 451648-28. The study is unacceptable for reasons listed below. The portion of the study conducted in Plot B is scientifically sound, but does not meet Subdivision N guidelines because the soil was not sampled deep enough to accurately define the extent of leaching of chlorothalonil and SDS-3701 under field conditions. These plots were later re-treated and planted for the purpose of obtaining rotational crop accumulation data, which is separately reported (DER 4 in this document).

1) **The data from Plot A do not serve to define a pattern or time course for the dissipation of chlorothalonil under field conditions.** The analytical results for soil samples taken from Plot A are too randomly variable to allow an accurate assessment of the dissipation of chlorothalonil and its degradates under field conditions. In addition, sampling was insufficient since soil was only sampled through day 29 following the tenth application, except for samples taken at 222 days posttreatment.

2) **The depth of soil sampling was insufficient to define the extent of leaching of chlorothalonil and its degradates.** At both treated plots, chlorothalonil was detected at up to 0.02 ppm in the 9- to 12-inch depth. The soil was not sampled at the 12- to 15-inch depth until 29 or 222 days posttreatment; it is possible that chlorothalonil may have been present in both plots at this depth prior to 29 days posttreatment. At Plot B, the soil was sampled to a depth of 36 inches at 540 days following the last application, at which time SDS-3701 was detected at an average of 0.01 ppm in the 15- to 18-inch depth. The soil should have been sampled at all sampling intervals to depths (preferably two sampling depths) at which residues were nondetectable.

3) The [*reviewer calculated*] observed half-life of 14-29 days was reported in this review. The study authors calculated a half-life of 9 days for chlorothalonil using data for the upper 12 inches of soil at Plot B at sampling intervals through day 35 following the last application. However, this conflicts with the data, since the chlorothalonil concentration in the upper 12 inches of soil at 14 days following the last treatment (0.04 ppm) was much greater than 50% of that present immediately following the last treatment (0.05 ppm). The authors did not use the data for plot A in calculating the half-life due to the

anomalously high residue level obtained for the 14-day soil sample (average of 0.43 ppm), and because the last sampling interval for this plot was only 29 days after the last application (except for one sample taken at 222 days following the last application).

4) Chlorothalonil residues in the soil were greater after four applications than after ten applications. The study authors suggested that this may be due to the broader foliage canopy that covered the soil during the later applications and prevented direct deposition of Bravo 720 on the soil.

5) A number of soil samples from the control plot (Plot C) contained detectable residues of chlorothalonil and its degradates. Maximum concentrations were 0.03 ppm of chlorothalonil, 0.09 ppm of SDS-3701, 0.006 ppm of HCB, and 0.009 ppm of PCBN (Table 9)

6) There were many other deficiencies:

    a) The original document was poorly organized and required extensive perusal on the part of the reviewer to obtain the pertinent information for review of the study. The methodology for the experiment was incomplete and was scattered throughout the document. Much of the information was reported in handwritten field records included in the original document. The registrant should have presented the details of the study in a more organized manner, so that the pertinent information could be readily obtained from the document.
    b) Field test data were incomplete.
    c) A complete description of the soil sampling procedures was not provided.
    d) The length of freezer storage time and the storage temperature of soil samples stored prior to analysis were not reported. In addition, freezer storage stability data were not provided.

Supplemental information which the study does provide includes the following:

1) Chlorothalonil was detected to a depth of 12-inches.

2) Chlorothalonil dissipated with an observed half-life of 14-29 days from the upper 12 inches of a plot of sandy loam soil that was treated at 10-day intervals with chlorothalonil (Bravo 720, 6 lb/gal FlC) at 1.12 lb ai/A/application ten times (total 11.2 lb ai/A).

3) The degradates occurred as follows:
4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) was isolated as deep as the 9- to 12-inch depth
2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525) was isolated as deep as the 3- to 6-inch depth
3-carboxy-2,5,6-trichlorobenzamide (SDS-46851), 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524), and

3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221) were isolated only in the 0-to 3-inch depth

4) The manufacturing impurities HCB and PCNB were isolated as deep as the 9- to 12-inch depth. The study authors stated that the levels of PCBN detected in soil from Plots A and B were related to the level of chlorothalonil residues present. The authors also concluded that the levels of HCB in the treated plots did not appear to be related to the Bravo 720 applications, since the concentrations of HCB were not significantly different than those detected in the control plot. In addition, pretreatment samples taken from the two treated plots contained detectable residues of HCB (0.003-0.006 ppm).

Greenfield, CA -- MRID# 415648-30. This study is unacceptable for reasons listed below. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of chlorothalonil and its degradates. Plot B was replanted to broccoli on April 28, 1987, and re-treated as part of a rotational crop study reported separately (DER 4 of this document).

1. **The cultural practices employed during the course of the study compromised study results.** Although "tillage of the soil is acceptable and recommended according to normal agricultural practices for the area and crop being planted", "all tillage operations should not disturb the soil at a depth exceeding 8 inches from the surface". At each of the treated plots, the broccoli crop was shredded and, as stated by the study author, "all chlorothalonil present on the foliage was transferred to the soil". The broccoli foliage was disked into the ground at Plot B but not at Plot A. The plots were disked 10-11 days after treatment. Both treated plots were subsequently chiseled to a depth of 14 inches. It is highly probable that these practices (cultivation, disking, and chiseling) resulted in movement of chlorothalonil residues to lower soil depths. Because the surface soil layers were mixed during the course of the study, the concentration of pesticide may have been diluted by bringing pesticide-free soil from lower horizons, and may have increased the rate of dissipation by aerating the soil and presenting new nutrient sources to the microbial population.

2) **Study results may also have been compromised by soil sampling procedures used.** A description of the technique, including sampling equipment used, was not provided; it was only stated that a soil sampling probe was used. The study author conceded that the presence of chlorothalonil at the 6- to 15-inch depths was likely due to tillage operations, adding that the sandy (loam) soil would be "quite susceptible to drag down of residues from upper levels by the sampling probe or mixing of levels when handling the probe". As stated by the study author, "because of these factors, it is not possible to clearly determine the soil mobility of chlorothalonil".

3) **Soil was not sampled deeply enough to define the extent of leaching of chlorothalonil and its degradates.** At both treated plots, chlorothalonil residues were detected in the 12- to 15-inch depth, the lowest soil depth sampled. At Plot A, concentrations of chlorothalonil and the degradate SDS-3701 in the 12- to 15-inch depth were up to 0.03 ppm and 0.02 ppm, respectively. At Plot B, chlorothalonil was detected at up to 0.12 ppm and SDS-3701 was detected at up to 0.03 ppm in the 12-to 15-inch depth. The soil should have been sampled to depths (preferably two sampling depths) at which residues were nondetectable.

4) The study author calculated a half-life of 40 days for chlorothalonil using residue data from the upper 12 inches of soil at Plots A and B. However, because of the inherent problems associated with this study, an accurate half-life determination for chlorothalonil cannot be made using these data. In addition, the author stated that the residue data from days 0 and 7 were not used due to the confounding effects of the cultural practices employed early in the study. The arbitrary exclusion of data used to calculate the half-life causes the resulting half-life to be of questionable value.

5) Other deficiencies include the following:

   a) The original document was poorly organized and required extensive perusal on the part of the reviewer to obtain the pertinent information for review of the study. The methodology for the experiment was incomplete and was scattered throughout the 360-page document. Much of the information was reported in handwritten field records included in the original document; these records were partially illegible and difficult to decipher.
   b) The length of freezer storage time, storage temperature of soil samples stored prior to analysis, and freezer storage stability data were not provided.
   c) A complete description of the soil sampling procedures was not provided.
   d) A description of the soil probe used to collect the soil samples, including type and diameter, was not reported.
   e) Field data, including meteorological data, were incomplete. In addition, irrigation data in the field records were partially illegible and difficult to decipher.
   f) It was not stated whether there was subsurface drainage.
   g) The pesticide and crop history at the test site prior to the initiation of the study was not reported. However, residues of chlorothalonil, its degradates, and manufacturing impurities (HCB and PCBN) were not detected in any control soil samples or in pretreatment samples taken from the two treated plots.

10.

Field Accumulation - Rotational Crops -- **MRID#s 415648-32 through -46**. This study cannot be used to fulfill data requirements at this time. Levels of chlorothalonil and its degradates in the soil immediately posttreatment and at planting and harvest of the rotational crops could not be adequately assessed because the data were not presented in a reviewable format. In order for this study to be reevaluated, the registrant must provide summarized soil residue data, complete site characteristics, and meteorological data. In addition, the lengths of time the samples were stored frozen and acceptable freezer storage stability data must be provided.

Ancillary Study - Freezer Storage Stability -- **MRID#s 415648-20 through -27**. This study cannot be used to fulfill data requirements. The experimental design used was not appropriate for determining the freezer storage stability of chlorothalonil and its degradates in the various plant matrices. Because the crops were field-treated, the initial quantity of chlorothalonil in each sample was variable, and degradation of chlorothalonil had already occurred prior to frozen storage. The appropriate method for determining the freezer storage stability of a test substance in a particular matrix involves spiking the matrix with a known amount of technical grade or purer test substance (chlorothalonil, SDS-3701, SDS-46851, HCB, or PCBN), then analyzing for the test substance and its degradates immediately posttreatment and after various lengths of time of frozen storage to determine if any degradation has occurred. Because the deficiencies cannot be resolved with the submission of additional data, a new study is required. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of chlorothalonil and its degradates.

8. RECOMMENDATIONS:

The data contained in this submission do not support removal of rotational crop restrictions at this time. Several other data requirements are unfulfilled, including photolysis in water, photolysis on soil, aerobic soil metabolism, and fish bioaccumulation. Some of this information is necessary to the proper execution and evaluation of the field studies, and should therefore be addressed before field studies are repeated. The soil photodegradation and aerobic soil metabolism data will be of particular interest. After relevant laboratory data are received and accepted, the applicant should initiate replacement studies for the requirements discussed in this submission. Due to findings of chlorothalonil degradates in ground water both monitoring and small scale prospective studies have been required (JHJ 10/31/90). To data no protocols or data have been received.

9. BACKGROUND:

A. Introduction

The status of data requirements is as follows:

hydrolysis -- fulfilled (MRID#s 00405-39,) stable at pH 5 and 7; 10% degrades in 30 days at pH 9; 2,4,5,6-tetra-Cl-isophthalimide the only degradate

photolysis in water -- **not** fulfilled (MRID #s 000872-81, 4018340-18, 000405-40, 1988 Reg. Std.) -- additional data are required -- MRID # 401834-18 could be made acceptable, and indicates stability to photolysis

soil photodegradation -- **not** fulfilled (MRID # 001437-51, 1988 Reg. Std)

aerobic soil metabolism -- **not** fulfilled -- the study (Guidelines subpart N) must establish patterns of disappearance of parent; appearance and disappearance of degradates; identity of degradates anaerobic soil metabolism -- fulfilled by acceptable anaerobic aqueous metabolism study (10/23/85, also HLB 4/22/86, MRID# 001479-75)

anaerobic aquatic metabolism -- fulfilled (10/23/85, also HLB 4/22/86, MRID# 001479-75) -- $t_{\frac{1}{2}}$ 5-15 days, producing 4-OH-2,5,6-tri-Cl-isophthalonitrile, 3-CN-2,4,5,6,-tetra-Cl-benzamide, 2-OH-5-CN-3,4,6-tri-Cl-benzamide, and 3-carboxy-2,5,6-trichlorobenzamide

leaching/adsorption/desorption -- fulfilled (8/1/86, MRID#s 001151-05, 001537-10) -- low leachability in lab, but findings in ground water triggered monitoring requirements. [k_ds 3 (sand) to 29 (silt) in batch studies.]

terrestrial field dissipation -- **partially** fulfilled (MRID # 000872-96, 1988 Reg. Std.) -- additional studies are discussed in this review

confined accumulation in rotational crops -- no further data required (1988 Reg. Std, MRID# 000294-09), field studies indicate the need for tolerances

field accumulation in rotational crops -- discussed in this review

fish bioaccumulation -- **not** fulfilled (EBC 11/29/89) -- possible accumulation

B. Directions for Use

Chlorothalonil is a broad spectrum nonsystemic protectant fungicide registered for use on terrestrial food crop, terrestrial nonfood, greenhouse food crop, greenhouse nonfood, domestic outdoor, forestry, and indoor use sites. Chlorothalonil is also used as a cotton seed treatment. Chlorothalonil may be formulated with carbaryl, sulfur, dicofol, dinocap, diazinon, fenaminosulf, and aromatic petroleum derivatives. Single active ingredient formulations of chlorothalonil consist of 5% D, 2.5-11.25% G, 26.5-75% WP, 55 WP/D, 20% Impr, 90% DF, 3.75-6% EC, and 4.5-54% FlC. Chlorothalonil may be applied using ground equipment, aircraft, or irrigation equipment.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: See attached DERs.

11. COMPLETION OF ONE-LINER: no information added

12. CBI APPENDIX: All data reviewed here are considered "company confidential" by the registrant and must be treated as such.

DATA EVALUATION RECORD

STUDY 1

CHEM 081901 Chlorothalonil 164-1

STUDY ID 415648-29 Formanik, J.B. 1989. Field-soil dissipation of residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), its soil metabolites and manufacturing impurities in soil from Bravo treated areas - Fresno, CA. 1986-1988. Document No. 1401-86-0084-CR-003. performed by Ricerca, Inc., Painesville, OH, and submitted by Fermenta ASC Corporation, Mentor, OH.

REVIEWED BY: J. Harlin TITLE: Staff Scientist
EDITED BY: K. Patten TITLE: Task Leader
T. Colvin-Snyder Staff Scientist
APPROVED BY: W. Spangler TITLE: Project Manager
ORG: Dynamac Corporation
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APPROVED BY: B. Conerly
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: E.B. Conerly 2/25/91

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study cannot be used to fulfill data requirements. Because the deficiencies cannot be resolved by submission of additional data, a new study is required. Since the data are considered to be of uncertain value, they should not be used to predict the environmental behavior of chlorothalonil and its degradates.

2. This study is unacceptable for reasons listed below. A more detailed discussion of deficiencies is given under "Reviewer's Comments".

    1. Despite sample compositing, which should minimize any variation, the data were too randomly variable to allow accurate assessment of the dissipation of chlorothalonil under field conditions. Possible contributing factors [*acknowledged by the study author*] include atypical cultural practices, problems with the soil sampling technique, and the lack of irrigation and rainfall during the later sampling intervals. Most movement of chlorothalonil residues in the 0- to 3- and 3- to 6-inch depths was attributed to cultivation and tillage prior to planting of the rotational crops.

    2. Although the study author reported a half-life of 58 days for chlorothalonil in the upper 12 inches of soil using ***selected*** data from both treated plots, an accurate half-life determination cannot be made due to the variability of the data. Since data for several sampling intervals were arbitrarily discarded for the half-life calculation, the calculated half-life is considered to be of questionable validity.

3. Soil sampling may not have gone deep enough to define the extent of leaching of chlorothalonil and its degradates. The soil should have been sampled at all sampling intervals to depths (preferably two sampling depths) at which residues were nondetectable.

4. Other deficiencies included the following:
    a) The original document was poorly organized and required extensive perusal on the part of the reviewer to obtain the pertinent information for review of the study. The registrant should have presented the details of the study in a more organized manner, so that the pertinent information could be readily obtained from the document.
    b) The length of freezer storage time and storage temperature of soil samples prior to analysis were not reported. Freezer storage stability data were not provided.
    c) Soil temperature data were not provided for any of the test plots.
    d) A number of soil samples taken from the control plot (Plot 3) contained detectable concentrations of HCB at all soil depths sampled.

METHODOLOGY:

Chlorothalonil (Bravo 500, 4.17 lb/gal FlC, Fermenta ACS) was broadcast sprayed onto two plots (Plots 1 and 2; each 60 x 90 feet) of sandy loam soil (58% sand, 32% silt, 10% clay, 0.4% organic matter, pH 6.6, CEC 5.3 meq/100 g) planted to tomatoes near Fresno, California, at 2.09 lb ai/A/application, eight times (total 16.78 lb ai/A) at weekly intervals. The tomatoes were planted 6/26/86; chlorothalonil applications began 8/16/86, using a tractor-mounted boom sprayer. An untreated control plot (Plot 3; 50 x 115 feet) was located ca. 215 feet from the treated plots.

Plot 2 and the control plot (Plot 3) were replanted to rotational crops of broccoli, carrots, leaf lettuce, onions, sugar beets, and wheat on November 14, 1986, and to tomatoes and cotton on April 9, 1987. Plot 1 was again treated eight times with chlorothalonil at 2.09 lb ai/A/application (total 16.78 lb ai/A) weekly, beginning July 10, 1987. Plot 1 and the control plot were replanted to broccoli, carrots, leaf lettuce, onions, sugar beets, and wheat on November 24, 1987, and to tomatoes and cotton on April 6, 1988. The planting and harvest dates for the rotational crops planted in each plot are provided in Tables III-V.

Soil samples were collected from both treated plots and the control plot prior to the first application in 1986; after the fourth and eighth applications; and at various intervals through 177 days following the last application.

At Plots 2 and 3, additional soil samples were taken prior to planting and at harvest of each rotational crop; and at 457-652 days following the last application.

At Plot 1, soil samples were also taken at 178, 222, 234, and 334 days after the last application made in 1987.

Ten soil cores were collected from each plot at each sampling interval using a zero-contamination probe[1]. Samples were collected to a depth of 12 inches through 14 days following the final treatment, and to a depth of 15 inches at later sampling intervals. Each soil sample was sectioned into 3-inch segments; segments from the same depth were composited, transferred into plastic bags, and frozen. The samples were then shipped frozen with dry ice to the analytical laboratory, where they were maintained frozen (temperature not reported) for an unspecified period of time prior to analysis. The soil samples were thawed and mixed by hand. Subsamples (20 g) of the soil were shaken with acetone:10 N sulfuric acid (95:5, v:v) for 2 hours, then centrifuged.

<u>Analysis for chlorothalonil by direct partitioning</u>: An aliquot (equivalent to 5 g of soil) of the extract was mixed with additional acetone:10 N sulfuric acid (95:5, v:v) and water, and partitioned twice with petroleum ether. The ether extracts from each partitioning were combined, mixed with keeper solution (2% paraffin oil in petroleum ether), concentrated in a water bath, and evaporated to dryness under a nitrogen stream. The resulting residues were dissolved in methylene chloride:hexane (20:80, v:v). Residues of chlorothalonil, and hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN), both described as manufacturing impurities of the test substance, were selectively partitioned on a Florisil column. Chlorothalonil was eluted from the column with $MeCl_2$:hexane (20:80); HCB was eluted with $MeCl_2$:hexane:acetonitrile (50:48.5:1.5); PCBN was eluted with 0.05% acetonitrile in hexane:methylene chloride (1:1, v:v). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The resulting residues were dissolved in toluene and analyzed for chlorothalonil, HCB, and PCBN using GC with ^{63}Ni electron-capture detection. Method detection limits were 0.01 ppm for chlorothalonil, 0.003 ppm for HCB, and 0.005 ppm for PCBN.

<u>Analysis for specific degradates by derivatization</u>: An aliquot of extract (equivalent to 10 g soil) was transferred to a beaker and mixed with keeper solution and water. The acetone in the extract was evaporated, a 0.4 M sodium carbonate solution was added to the extract and the pH was adjusted to 4.5. The acidified extract was partitioned twice with petroleum ether; both ether phases were discarded. The extracted aqueous phase was adjusted to pH <2, and sodium chloride was added to obtain a 30% solution (w:v). The solution was partitioned twice with water and diethyl ether. The diethyl ether phases were combined and mixed with keeper solution, and the solution was concentrated in a water bath and evaporated to dryness under a nitrogen stream. Resulting residues were dissolved in acetone; the resulting solution was divided into two equal portions. Each portion was concentrated and dried as described above.

One portion was used to derivatize the degradates 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701), 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525), and 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851) into their methyl ether and methyl ester derivatives.[2] Later (length of storage not specified), the

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[1] A 3/4-inch diameter probe was used through 60 days after the last application and a 1-inch diameter probe was used at later sampling intervals.

[2] Concentrated HCL:methanol (1:3, v:v) and diazopropane solution was added to the dried residue, and the solution was allowed to sit in a fume hood at ambient temperature for 1 hour, after which the solvent was evaporated under a nitrogen stream. The residues were dissolved in methylene chloride and refrigerated.

derivatized sample was filtered through a glass chromatographic column. Derivatized SDS-3701 was eluted from the column with methylene chloride, and derivatized SDS-47525 and SDS-46851 were eluted with acetone:methylene chloride (50:50). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The dried [^{14}C]residues were dissolved in toluene and quantified using GC with ^{63}Ni electron-capture detection. The method detection limits were 0.01 ppm for SDS-3701, and 0.03 ppm for SDS-46851 and SDS-47525.

The second portion was used for separation and cleanup of the degradates 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524) and 3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221). The dried residues were dissolved in methylene chloride; some portions were diluted with toluene and analyzed directly using GC with ^{63}Ni electron-capture detection. The remaining methylene chloride solutions were filtered through a glass chromatographic column. The column was eluted with methylene chloride, which was discarded, followed by acetone:methylene chloride (50:50). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The dried [^{14}C]residues were dissolved in toluene and quantified using GC with ^{63}Ni electron-capture detection. The method detection limits were 0.03 ppm for SDS-47523/24 and SDS-19221.[3]

DATA SUMMARY:

There was no discernible pattern of dissipation of Chlorothalonil in two field plots of sandy loam soil planted to tomatoes located near Fresno, California, that were treated with chlorothalonil (Bravo 500, 4.17 lb/gal FlC) at 2.09 lb ai/A/application at weekly intervals eight or 16 times (total 16.78 or 33.56 lb ai/A) during 1986-87. Chlorothalonil was detected to the 15- to 18-inch depth, the deepest layer sampled. One degradate, 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701), was detected in all soil layers; no other degradates were detected (except for one isolated detection of 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851) in the upper 3 inches of one plot). Hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN), reported to be manufacturing impurities of the test substance, were detected to depths of 15 and 6 inches, respectively.

One plot (Plot 1) was treated with eight applications beginning in August 1986, and eight additional applications beginning in July 1987; each set of treatments was made at 7-day intervals. The plot was replanted to rotational crops of broccoli, carrots, leaf lettuce, onions, sugar beets, and wheat in November 1987, and to tomatoes and cotton in April 1988. Following the first set of treatments in 1986, the average concentration of chlorothalonil in the 0- to 3-inch soil depth was 0.44 ppm immediately following the fourth application, 0.25 ppm immediately following the eighth application, 0.50-1.85 ppm at 7-30 days following the eighth application, 0.25-0.44 ppm at 60-120 days following the eighth application, and 0.07 ppm at 177 days following the eighth application (Table 9). In deeper soil

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[3] To determine the validity of the method, fortified soil samples were analyzed. Recoveries from fortified soil samples were 63-127% for chlorothalonil, 61-126% for SDS-3701, 62-130% for SDS-47525, 63-136% for SDS-46851, 68-125% for SDS-19221, 62-125% for SDS-47523, 60-130% for HCB, and 73-133% for PCBN. Fortification levels were 0.03-5.0 ppm for chlorothalonil; 0.03-1.0 ppm for SDS-3701; 0.06-2.0 ppm for SDS-47525, SDS-46851, SDS-19221, and SDS-47523; 0.01-0.05 ppm for HCB; and 0.015-0.10 ppm for PCBN.

layers, maximum average concentrations of chlorothalonil were 0.24 ppm in the 3- to 6-inch depth, 0.02 ppm in the 6- to 9-inch depth, 0.03 ppm in the 9- to 12-inch depth, and 0.01 ppm in the 12- to 15-inch depth.

The degradate

4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701)

was a maximum of 0.18 ppm in the 0- to 3-inch depth (at 120 days following the eighth application), 0.09 ppm in the 3- to 6-inch depth, 0.03 ppm in the 6- to 9-inch depth, and was <0.01 ppm (not detected) below 9 inches. The degradates

2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525),

3-carboxy-2,5,6-trichlorobenzamide (SDS-46851),

3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524), and

3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221)

were <0.03 ppm (not detected) in any soil samples. The manufacturing impurity HCB was ≤0.007 ppm in the 0- to 3- and 3- to 6-inch depths, and PCBN was a maximum of 0.033 ppm and 0.014 ppm in the 0- to 3- and 3- to 6-inch depths, respectively. Neither of these manufacturing impurities was detected (<0.003 ppm) below 6 inches.

Following the second set of eight applications made to Plot 1 in 1987, average concentrations of chlorothalonil at 178-334 days after the last application (the only days sampled) were 0.09-0.23 ppm in the 0- to 3-inch depth, ≤0.04 ppm in the 3- to 6-inch depth, and <0.01 ppm (not detected) below 6 inches (Table 9). The degradate SDS-3701 was detected to the lowest sampling depth of 12 to 15 inches; SDS-3701 was a maximum of 0.42-0.45 ppm in the 0- to 3- and 3- to 6-inch depths and was ≤0.10 below the 6-inch depth. No other degradates were detected. HCB and PCBN were detected in the 0- to 3-inch depth at maximum concentrations of 0.003 and 0.010 ppm, respectively, and were not detected below the 3-inch depth.

A second plot (Plot 2) was treated with eight applications of chlorothalonil at 7-day intervals beginning in August 1986. The plot was replanted to broccoli, carrots, leaf lettuce, onions, sugar beets, and wheat in November 1986, and to tomatoes and cotton in April 1987. In the 0- to 3-inch depth, average concentrations of chlorothalonil were 1.79 ppm following the fourth application, 2.04 ppm following the eighth application, 1.40 ppm at 7 days following the eighth application, 0.26-0.43 ppm at 14-90 days following the eighth application, 0.09-0.42 ppm at 120-177 days following the eighth application, 0.02-0.20 ppm at 185-457 days following the eighth application, and 0.42-0.44 ppm at 547-652 days following the eighth application (Table 10). At deeper soil depths, chlorothalonil was a maximum of 0.22 ppm in the 3- to 6-inch depth, 0.04 ppm in the 6- to 9- and 9- to 12-inch depths, and 0.01 ppm in the 12- to 15-inch depth. Maximum concentrations of the degradate SDS-3701 were 0.63 ppm in the 0- to 3-inch depth (at 652 days following the last application), 0.44 ppm in the 3- to 6-inch depth, 0.14 ppm in the 6- to 9-inch depth, 0.08 ppm in the 9- to 12-inch depth, and 0.05 ppm in the 12- to 15-inch depth. The degradates SDS-47525, SDS-47523/SDS-47524 and SDS-19221 were <0.03 ppm (not detected) in all soil samples. The degradate SDS-46851 was <0.03 ppm (not detected) at all sampling intervals except for an isolated detection of 0.16 ppm (average) at 652 days following the last application. HCB was detected at all sampling depths (≤0.008 ppm). PCBN was isolated at up to 0.038

ppm in the 0- to 3-inch depth and 0.014 ppm in the 3- to 6-inch depth; PCNB was not detected below the 6-inch depth.

During the study period for Plots 1 and 2, air temperatures ranged from 22 to 107 F; soil temperatures were not reported. When sampling was terminated at each plot, cumulative precipitation plus irrigation totaled 88.4 inches at Plot 1 and 63.9 inches at Plot 2. The slope of the field was <0.5%, the depth to the water table was approximately 49 feet, and there was no subsurface drainage in place.

COMMENTS:

1. EFGWB strongly prefers that there be at least three independent specimens to represent each data point. This appears not to have been the case in this study. Despite this compositing which should minimize any variation, the data were too variable to accurately assess the dissipation of chlorothalonil under field conditions. Possible contributing factors [*acknowledged by the study author*] include atypical cultural practices, problems with the soil sampling technique, and the lack of irrigation and rainfall during the later sampling intervals. Most movement of chlorothalonil residues in the 0- to 3- and 3- to 6-inch depths was attributed to cultivation and tillage prior to planting of the rotational crops. The presence of chlorothalonil residues in the lower sampling depths could have been due to contamination from upper soil layers during soil sampling. The study author stated that data obtained from Plot 2 after the 360-day sampling interval were of questionable value since no irrigation was applied to the test area from days 360-652 following the last application, and only 5.5 inches of rain fell during the 6-month period. The highly variable results obtained for each treated plot were possibly due to a combination of problems associated with the soil sampling techniques and atypical cultural practices.

2. Although the study author reported a half-life of 58 days for chlorothalonil in the upper 12 inches of soil using ***selected*** data from both treated plots, an accurate half-life determination cannot be made due to the variability of the data. Calculations were done using residue data for plot 1 at 30-177 days following the first application and for plot 2 at 0-163 days posttreatment. The author stated that the residue data for plot 1 at 0-30 days and for plot 2 at 177 days and beyond were not used in calculating the half-life because the residue levels were unusually high at these sampling intervals. Since data for several sampling intervals were arbitrarily discarded for the half-life calculation, the calculated half-life is considered to be of questionable validity.

3. Soil sampling may not have gone deep enough to define the extent of leaching of chlorothalonil and its degradates. Chlorothalonil was detected at 0.01 ppm (average) in the lowest sampling depth of 12 to 15 inches at 120 days following the last application made in 1986 at Plot 1, and at 318 days following the last application at Plot 2 (Tables 9 and 10). In addition, soil was not sampled at 12- to 15-inch depth until 30 days posttreatment; it is possible that chlorothalonil may have been present in both plots at this depth prior to 30 days posttreatment. The soil should have been sampled at all sampling intervals to depths (preferably two sampling depths) at which residues were nondetectable.

4. The length of freezer storage time and storage temperature of soil samples prior to analysis were not reported. Also, freezer storage stability data were not provided. Freezer storage stability data should be provided for the longest period of freezer storage.

5. Soil temperature data were not provided for any of the test plots.

6. The data summarized in this review were obtained from Summary Tables 9-11 of the original document and are the mean residues of the major compounds found in the soil samples.

7. A number of soil samples taken from the control plot (Plot 3) contained detectable concentrations of HCB (average concentrations of 0.003-0.009 ppm) at all soil depths sampled (Table 11). Since the concentrations of HCB were not significantly different in the treated soil, the author concluded that they did not appear to be related to the application of Bravo 500. Chlorothalonil residues were not detected in any pretreatment soil samples taken from treated plots.
8. The study author stated that levels of PCBN found in soil from Plots 1 and 2 were related to the level of chlorothalonil residues present.
9. Plot maintenance for the primary tomato and secondary plantings consisted of thinning, transplanting, and weeding. The following pesticides were applied to the rotational crops: Fusilade 4E at 12.0 oz/A to lettuce, broccoli, onions, sugar beets, and carrots in plots 2 and 3 on January 12, 1987; Caparol 4L at 2.5 pints/A applied to cotton in plots 2 and 3 on April 9, 1987; Tillam 7E at 2.5 pints/A to tomatoes in plots 2 and 3 on April 9, 1987; Kelthane 4E to cotton in plots 2 and 3 on June 1, 1987; and, a 1% solution of Round-up to unplanted cotton and tomato beds in plots 1 and 3 on March 3, 1988. No pesticides were used at the study site for five years prior to the initiation of the study.

10. The second-year applications made to Plot 1 were intended for use in a rotational crop study. The study author stated that soil samples from the second-year applications were not assayed, except for soil sampled at 222, 234, and 334 days after the last application as requested by the sponsor. These soil data are summarized in this review. The data for the rotational crop study are provided in separate documents, and are reviewed in Study 4 of this report.

11. The original document was poorly organized and required extensive perusal on the part of the reviewer to obtain the pertinent information for review of the study. The methodology for the experiment was scattered throughout the document. The registrant should have presented the details of the study in a more organized manner, so that the pertinent information could be readily obtained from the document.

CHLOROTHALONIL Sh# 081901

Page_____ is not included in this copy.

Pages 20 through 35 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.

X____ 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.

DATA EVALUATION RECORD

STUDY 2

CHEM 081901 Chlorothalonil 164-1

FORMULATION--14--FLOWABLE CONCENTRATE

STUDY ID 45164828 -- Rose, C.A., and D.L. Ballee. 1988. Determination of residues (field-soil dissipation) of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), its soil metabolites and manufacturing impurities in soil from Bravo treated areas - Donalsonville, GA. 1986-1988. Document No. 1401-86-0084-CR-002. Unpublished study performed by Ricerca, Inc., Painesville, OH, and submitted by Fermenta ASC Corporation, Mentor, OH.

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EDITED BY: K. Patten TITLE: Task Leader
T. Colvin-Snyder Staff Scientist
APPROVED BY: W. Spangler TITLE: Project Manager
ORG: Dynamac Corporation
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APPROVED BY: B. Conerly
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: E. B. Conerly 2/25/91

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study cannot be used to fulfill data requirements. The problems with this study cannot be resolved with the submission of additional data. A new study must be conducted.

2. The portion of the study conducted in Plot A is unacceptable for the reasons listed below. A more detailed discussion is given in "Reviewer's Comments".

   1. The depth of soil sampling was insufficient to define the extent of leaching of chlorothalonil and its degradates. The soil should have been sampled at all sampling intervals to depths (preferably two sampling depths) at which residues were nondetectable.

   2. The analytical results for soil samples taken from Plot A are too variable to allow an accurate assessment of the dissipation of chlorothalonil and its degradates under field conditions. In addition, sampling was insufficient since soil was only sampled through day 29 following the tenth application, except for samples taken at 222 days posttreatment.

   3. The study authors calculated a half-life of 9 days for chlorothalonil using data for the upper 12 inches of soil at Plot B at sampling intervals through day 35 following the last application. However, the calculated half-life conflicts with the data, since the chlorothalonil concentration in the upper

12 inches of soil at 14 days following the last treatment (0.04 ppm) was much greater than 50% of that present immediately following the last treatment (0.05 ppm). Therefore, the observed half-life of 14-29 days was reported in this review. In addition, the authors stated that the data for plot A were not used in calculating the half-life for several reasons.

4. Other deficiencies include the following:

   a) Length of freezer storage time and the storage temperature of soil samples stored prior to analysis were not reported, and freezer storage stability data were not provided.
   b) Field test data were incomplete. The slope of the field and depth to the water table were not provided, and the report did not state whether subsurface drainage was in place. In addition, soil temperature and meteorological data were incomplete.
   c) Complete description of the soil sampling procedures was not provided. A description of the soil probe used to collect the soil samples, including the type and diameter of the probe, was not reported.
   d) Total ppm values for the 0- to 12-inch soil depth reported in Table 1 are in error; these values need to be divided by four to obtain the correct values.
   e) Clorothalonil residues in the soil were greater after four applications than after ten applications. The study authors suggested that this may be due to the broader foliage canopy that covered the soil during later applications.

5. The original document was poorly organized and required extensive perusal on the part of the reviewer to obtain the pertinent information for review of the study. The methodology for the experiment was incomplete and was scattered throughout the document. Much of the information was reported in handwritten field records included in the original document. The registrant should have presented the details of the study in a more organized manner, so that the pertinent information could be readily obtained from the document.

The portion of the study conducted in Plot B is scientifically sound, but does not meet Subdivision N guidelines because the soil was not sampled deep enough to accurately define the extent of leaching of chlorothalonil and SDS-3701 under field conditions; and freezer storage stability data and the conditions of frozen storage for the field soil samples were not provided.

3. Supplemental information which the study does provide includes the following:

   1) Chlorothalonil was detected to a depth of 12-inches.

   2) Chlorothalonil dissipated with an observed half-life of 14-29 days from the upper 12 inches of a plot of sandy loam soil that was treated at 10-day intervals with chlorothalonil (Bravo 720, 6 lb/gal FlC) at 1.12 lb ai/A/application ten times (total 11.2 lb ai/A).

   3) The degradates occurred as follows:
      4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) was isolated as deep as the 9- to 12-inch depth

2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525) was isolated as deep as the 3- to 6-inch depth

3-carboxy-2,5,6-trichlorobenzamide (SDS-46851), 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524), and 3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221) were isolated only in the 0- to 3-inch depth

4) The manufacturing impurities HCB and PCNB were isolated as deep as the 9- to 12-inch depth.

METHODOLOGY:

Chlorothalonil (Bravo 720, 6 lb/gal FlC, Fermenta ACS) was broadcast sprayed onto two plots (Plots A and B; each 36 x 100 feet) of sandy loam soil (70% sand, 15% silt, 15% clay, 2.1% organic matter content, pH 5.3, CEC 2.4 meq/100 g) planted to peanuts near Donalsonville, Georgia, at 1.12 lb ai/A/application ten times (total 11.2 lb ai/A) at 10-day intervals. The plots were planted to peanuts on May 23, 1986, and the chlorothalonil applications began on June 20, 1986, using a tractor-mounted boom sprayer. The two treated plots were spaced 12 feet apart. An untreated plot (Plot C; 36 x 100 feet) located 12 feet from Plot B served as the control.

The peanuts in each plot were dug on September 30 and harvested on October 2, and the plots were disked on October 14, 1986. Portions of Plots B and C were planted to cabbage, turnips, and winter wheat on October 22, 1986; to field corn on March 17, 1987; to peanuts, grain sorghum, sweet potatoes, and summer squash on April 28, 1987; and to soybeans and cotton on May 29, 1987. The rotational crops were harvested between July 6 and November 6, 1987.

Soil samples were collected from Plot A prior to the first application, following the fourth and tenth applications, at various intervals through day 29 following the last application, and at 222 days following the last application. Soil samples were collected from Plot B and the control plot (Plot C) prior to the first application, after the fourth and tenth applications, and at various intervals through 540 days following the last application. Ten soil cores were collected from each plot at each sampling interval; sampling procedures were not described. Soil cores were taken to a depth of 12 inches through 29 days following the last application, and to a depth of 15 inches at later sampling intervals. The soil samples were shipped frozen with dry ice to the analytical laboratory, where they were maintained frozen (temperature not reported) for an unspecified period of time prior to analysis.

The soil samples were thawed and mixed by hand. Subsamples (20 g) of the soil were extracted with acetone:10 N sulfuric acid (95:5, v:v) on a reciprocating shaker for 2 hours, then centrifuged.

<u>Analysis for chlorothalonil by direct partitioning</u>: An aliquot (equivalent to 5 g of soil) of the extract was mixed with additional acetone:10 N sulfuric acid (95:5, v:v) and water, and partitioned twice with petroleum ether. The two ether extracts were combined, mixed with keeper solution (2% paraffin oil in petroleum ether), concentrated in a water bath, and evaporated to dryness under a nitrogen stream. The resulting residues were dissolved in $MeCl_2$:hexane (20:80, v:v). Residues of chlorothalonil, and of hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN), both described as manufacturing impurities of the test substance, were selectively partitioned on a Florisil column. Chlorothalonil

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was eluted from the column with $MeCl_2$:hexane (20:80); HCB was eluted with $MeCl_2$:hexane:acetonitrile (50:48.5:1.5); PCBN was eluted with 0.05% acetonitrile in hexane:$MeCl_2$ (1:1, v:v). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The resulting residues were dissolved in toluene and analyzed for chlorothalonil, HCB, and PCBN using GC with ^{63}Ni electron-capture detection. The method detection limits were 0.01 ppm for chlorothalonil, 0.003 ppm for HCB, and 0.005 ppm for PCBN.

Analysis for specific degradates by derivatization: An aliquot of the extract (equivalent to 10 g of soil) was transferred to a beaker and mixed with keeper solution and water. The acetone in the extract was evaporated either by placing the beaker in a waterbath with a stream of dry air impinging on the solvent surface or by allowing the solution to stand overnight at room temperature in a fume hood. After the acetone was evaporated, a 0.4 M sodium carbonate solution was added to the extract and the pH was adjusted to 4.5. The acidified extract was partitioned twice with petroleum ether by manual shaking for 2 minutes; both ether phases were discarded. The extracted aqueous phase was adjusted to pH <2, and sufficient sodium chloride was added to the solution to obtain a 30% solution (w:v). The solution was partitioned twice with water and diethyl ether by manual shaking for 2 minutes. The diethyl ether phases were combined and mixed with keeper solution, and the solution was concentrated in a water bath and evaporated to dryness under a nitrogen stream. The residues were dissolved in acetone, and the resulting solution was divided into two equal portions. Each portion was concentrated and dried as described above.

One portion was used to derivatize the degradates 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701), 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525), and 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851) into their methyl ether and methyl ester derivatives.[1] Later (length of storage not specified), the derivatized sample was filtered through a glass chromatographic column. Derivatized SDS-3701 was eluted from the column with $MeCl_2$, and derivatized SDS-47525 and SDS-46851 were eluted with acetone:$MeCl_2$ (50:50). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The dried [^{14}C]residues were dissolved in toluene and quantified using GC with ^{63}Ni electron-capture detection. The method detection limits were 0.01 ppm for SDS-3701, and 0.03 ppm for SDS-46851 and SDS-47525.

The second portion was used for separation and cleanup of the degradates 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524) and 3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221). The dried residues were dissolved in $MeCl_2$; some portions were diluted with toluene and analyzed directly using GC with ^{63}Ni electron-capture detection. The remaining $MeCl_2$ solutions were filtered through a glass chromatographic column. The column was eluted with $MeCl_2$, which was discarded, followed by acetone:$MeCl_2$ (50:50). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The dried [^{14}C]residues were dissolved in toluene and

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[1] Concentrated HCL:methanol (1:3, v:v) and diazopropane solution was added to the dried residue, and the solution was allowed to sit in a fume hood at ambient temperature for 1 hour, after which the solvent was evaporated under a nitrogen stream. The residues were dissolved in $MeCl_2$ and refrigerated.

quantified using GC with ^{63}Ni electron-capture detection. The method detection limits were 0.03 ppm for SDS-47523/24 and SDS-19221.[2]

DATA SUMMARY:

Chlorothalonil dissipated with an observed half-life of 14-29 days from the upper 12 inches of a plot (Plot B) of sandy loam soil that was treated at 10-day intervals with chlorothalonil (Bravo 720, 6 lb/gal FlC) at 1.12 lb ai/A/application (1.5 pints/A/application) ten times (total 11.2 lb ai or 15.0 pints/A). The plot, which was planted to peanuts and located near Donalsonville, Georgia, was treated beginning June 20, 1986; Plot B was also planted to rotational crops during the study period (1987-88). The average concentrations of chlorothalonil in the 0- to 3-inch depth were 0.23 ppm immediately following the fourth application, 0.21 ppm immediately following the tenth application, 0.13 ppm at 14 days following the tenth application, 0.07 ppm at 29 days following the tenth application, and ≤0.01 ppm by 222 days following the tenth application (Table 11). At deeper soil depths, the average chlorothalonil concentrations were ≤0.02 ppm at the 3- to 6-, 6- to 9-, and 9- to 12-inch depths, and <0.01 ppm (not detected) in the 12- to 15-inch depth (sampled after 35 days following the last treatment). Maximum concentrations of the degradate

4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701)

were 0.22 ppm in the 0- to 3-inch depth (immediately following the fourth treatment), 0.07 ppm in the 3- to 6- and 6- to 9-inch depths, 0.01 ppm in the 9- to 12-inch depth, and <0.01 ppm (not detected) in the 12- to 15-inch depth (except for one isolated detection of 0.01 ppm at 540 days after the last application). The degradates

2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525),

3-carboxy-2,5,6-trichlorobenzamide (SDS-46851),

3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524), and

3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221)

were detected at average concentrations of up to 0.04 or 0.05 ppm in the upper 3 inches of soil, and were <0.03 ppm (not detected) below the 3-inch depth, except for SDS-47525, which was isolated at 0.04 ppm in the 3- to 6-inch depth at 14 days following the tenth application. In the upper 3 inches of soil, HCB and PCNB, reported to be manufacturing impurities, reached maximum concentrations of 0.008 ppm and 0.016 ppm, respectively; HCB and PCNB were detected in the 3- to 6-, 6- to 9-, and 9- to 12-inch depths at up to 0.007 ppm and 0.009 ppm, respectively.

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[2] To determine the validity of the method, fortified soil samples were analyzed. Recoveries from fortified soil samples were 60-137% for chlorothalonil, 60-133% for SDS-3701, 60-147% for SDS-47525, 60-140% for SDS-46851, 61-143% for SDS-19221, 62-135% for SDS-47523, 70-140% for HCB, and 60-128% for PCBN. Fortification levels were 0.03-15 ppm for chlorothalonil; 0.03-0.50 ppm for SDS-3701; 0.06-0.50 ppm for SDS-47525, SDS-46851, SDS-19221, and SDS-47523; 0.01-0.05 ppm for HCB; and 0.015-0.10 ppm for PCBN.

During the study period for Plot B, air temperatures ranged from 21.4 to 102 F, and soil temperatures (3-inch depth) ranged from 31.6 to 115.9 F. When sampling was terminated at the plot, precipitation totaled 82.6 inches and irrigation totaled 12.75 inches.

In a second plot of sandy loam soil (Plot A) that was treated the same way as Plot B, except that rotational crops were not planted, the concentration of chlorothalonil was variable with no discernible pattern of dissipation. In the 0- to 3-inch depth, the average concentration of chlorothalonil was 0.47 ppm immediately following the fourth application, 0.19 ppm immediately following the tenth application, 0.27-0.43 ppm at 7-14 days following the tenth application, and 0.05-0.06 ppm at 29-222 days following the tenth application (Table 10). At deeper sampling depths, average concentrations of chlorothalonil were ≤0.03 ppm in the 3- to 6-inch depth and ≤0.02 ppm in the 6- to 9- and 9- to 12-inch depths. The degradate SDS-3701 was a maximum of 0.23 ppm in the 0- to 3-inch depth at 14 days following the last application and 0.03 ppm in the 3- to 6-inch depth; SDS-3701 was <0.01 ppm (not detected) below 6 inches, except for one detection of 0.01 ppm in the 9- to 12-inch depth immediately after the fourth application. The degradates SDS-46851, SDS-47523/SDS-47524, and SDS-19221 were detected at up to 0.04 or 0.05 ppm in the 0- to 3-inch depth, and were <0.03 ppm (not detected) below 3 inches. The degradate SDS-47525 was <0.03 ppm (not detected) in all soil samples. The manufacturing impurity HCB was ≤0.003 ppm in all soil samples. PCBN was a maximum of 0.015 ppm in the upper 3 inches, and was <0.003 ppm (not detected) below the 3-inch depth.

During the study period for Plot A, air temperatures ranged from 47.2 to 102 F up to 29 days after the last application and were 25.1-102 F from 29-222 days after the last application. During the entire study period, soil temperatures (3-inch depth) ranged from 35.6 to 95 F. Precipitation totaled 9.36 inches at 29 days after the last application, and approximately 38 inches at 222 days after the last application; irrigation totaled 3.0 inches during the entire study period.

COMMENTS:

1. The depth of soil sampling was insufficient to define the extent of leaching of chlorothalonil and its degradates. At both treated plots, chlorothalonil was detected at up to 0.02 ppm in the 9- to 12-inch depth. The soil was not sampled at the 12- to 15-inch depth until 29 or 222 days posttreatment; it is possible that chlorothalonil may have been present in both plots at this depth prior to 29 days posttreatment. At Plot B, the soil was sampled to a depth of 36 inches at 540 days following the last application, at which time SDS-3701 was detected at an average of 0.01 ppm in the 15- to 18-inch depth. The soil should have been sampled at all sampling intervals to depths (preferably two sampling depths) at which residues were nondetectable.

2. The analytical results for soil samples taken from Plot A are too variable to allow an accurate assessment of the dissipation of chlorothalonil and its degradates under field conditions. In addition, sampling was insufficient since soil was only sampled through day 29 following the tenth application, except for samples taken at 222 days posttreatment.

3. The length of freezer storage time and the storage temperature of soil samples stored prior to analysis were not reported. In addition, freezer storage stability

data were not provided. Freezer storage stability data should be provided for the longest period of freezer storage.

4. Field test data were incomplete. The slope of the field and depth to the water table were not provided, and the report did not state whether subsurface drainage was in place. In addition, soil temperature data were incomplete; data were not provided for June 20 through August 1986. Meteorological data from June 20 through August 1986 of the study period were obtained from the Bainbridge weather station, located 25 miles from the test site. It is highly desirable that meteorological data for the study period be obtained at the test site since rainfall and temperatures can vary between sites in close proximity.

5. A complete description of the soil sampling procedures was not provided. A description of the soil probe used to collect the soil samples, including the type and diameter of the probe, was not reported.

6. The data summarized in this review were obtained from Summary Tables 9-11 of the original document and are the mean residues of the major compounds found in the soil samples.

7. The study authors calculated a half-life of 9 days for chlorothalonil using data for the upper 12 inches of soil at Plot B at sampling intervals through day 35 following the last application. However, the calculated half-life conflicts with the data, since the chlorothalonil concentration in the upper 12 inches of soil at 14 days following the last treatment (0.04 ppm) was much greater than 50% of that present immediately following the last treatment (0.05 ppm). Therefore, the observed half-life of 14-29 days was reported in this review.

   In addition, the authors stated that the data for plot A were not used in calculating the half-life due to the anomalously high residue level obtained for the 14-day soil sample (average of 0.43 ppm), and because the last sampling interval for this plot was only 29 days after the last application (except for one sample taken at 222 days following the last application).

8. Total ppm values for the 0- to 12-inch soil depth reported in Table 1 are in error; these values need to be divided by four to obtain the correct values.

9. Chlorothalonil residues in the soil were greater after four applications than after ten applications. The study authors suggested that this may be due to the broader foliage canopy that covered the soil during the later applications and prevented direct deposition of Bravo 720 on the soil. The peanut crop grew from 3 inches at the first application to 8-10 inches at the fourth application, and was 20 inches tall at the nutfill stage by the tenth application.

10. The study authors stated that the levels of PCBN detected in soil from Plots A and B were related to the level of chlorothalonil residues present. The authors also concluded that the levels of HCB in the treated plots did not appear to be related to the Bravo 720 applications, since the concentrations of HCB were not significantly different than those detected in the control plot. In addition, pretreatment samples taken from the two treated plots contained detectable residues of HCB (0.003-0.006 ppm).

11. A number of soil samples from the control plot (Plot C) contained detectable residues of chlorothalonil and its degradates. Maximum concentrations were 0.03

ppm of chlorothalonil, 0.09 ppm of SDS-3701, 0.006 ppm of HCB, and 0.009 ppm of PCBN (Table 9).

12. Plot maintenance during the study period included fertilizing, weeding, and disking. The plots were treated with post emergence applications of Fusilade 2000 (24 oz) plus Blazer at 0.25 lb ai/A plus Crop Oil Concentrate on June 20, 1986, followed by Poast and COC at 16 oz plus 1 qt/A on July 23, 1986, to control weeds. The plots received one shallow cultivation on June 30, 1986. The pesticide and crop history at the test site prior to the initiation of the study was not reported.

13. As part of a rotational crop study, Plot A was replanted to peanuts on April 28, 1987, and retreated with eight additional applications of Bravo 720 at 1.5 pints/A (total 12.0 pints/A), made at 10-day intervals, beginning June 1, 1987. At later dates, Plot A and the control plot (Plot C) were replanted to rotational crops. The data for the rotational crop study are provided in separate documents, and are reviewed in Study 4 of this report.

14. The original document was poorly organized and required extensive perusal on the part of the reviewer to obtain the pertinent information for review of the study. The methodology for the experiment was incomplete and was scattered throughout the document. Much of the information was reported in handwritten field records included in the original document. The registrant should have presented the details of the study in a more organized manner, so that the pertinent information could be readily obtained from the document.

CHLOROTHALONIL Sh# 081901

Page_____ is not included in this copy.

Pages 44 through 56 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.

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____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

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DATA EVALUATION RECORD

STUDY 3

CHEM 081901 Chlorothalonil 164-1

FORMULATION--14--FLOWABLE CONCENTRATE

STUDY ID 41564830 -- King, C. 1989. Field-soil dissipation of residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), its degradation products, and manufacturing impurities in soil from Bravo-treated areas - Greenfield, CA. 1986-1988. Doc. No. 1401-86-0084-CR-004. Unpublished study performed by Ricerca, Inc., Painesville, OH, and submitted by Fermenta ASC Corporation, Mentor, OH.

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ORG: EFGWB/EFED/OPP

SIGNATURE: E. B. Conerly 12/21/90

CONCLUSIONS:

Dissipation - Terrestrial Field

1. This study cannot be used to fulfill data requirements. The deficiencies cannot be resolved with the submission of additional data. A new study must be conducted. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of chlorothalonil and its degradates.

3. This study is unacceptable for the following reason:

    Cultural practices employed during this study were such that the results are compromised. Dissipation of chlorothalonil in soil can not be accurately assessed because the surface soil layers were mixed during the course of the study. This appears to have diluted the concentration of pesticide by bringing pesticide-free soil from lower horizons, and may have increased the rate of dissipation by aerating the soil and presenting new nutrient sources to the microbial population.

METHODOLOGY:

Chlorothalonil (Bravo 500, 4.17 lb/gallon FlC, Fermenta ACS) was broadcast sprayed onto two 0.5-acre field plots (Plots A and B) of sandy loam soil (68.4% sand, 27.2% silt, 2.4% clay, 0.21% organic matter, pH 6.6, CEC 14 meq/100 g) planted to broccoli near Greenfield, California, at 0.63 lb ai/A/application (2.25 pints/A/application) nine times (total 5.7 lb ai or 20.25 pints/A) at weekly intervals. The plots were planted to broccoli on July 11, 1986, and the chlorothalonil applications were made between August 13 and October 7, 1986, using a hydraulic boom sprayer. The two treated plots were located adjacent to one another and were separated by a buffer row (width not reported). An untreated plot (Plot C; 0.25 acres) located north of the treated plots served as the control; a road separated the control plot from the treated plots. The broccoli crop was shredded at the three plots on October 17, 1986; the broccoli foliage was disked into the ground at Plots B and C on October 18, but not at Plot A. Both treated plots (Plots A and B) were subsequently chiseled to a depth of 14 inches; Plot B was chiseled on October 28, 1986, and Plot A was chiseled on April 4, 1987 (179 days after the last application).

Soil samples were taken from the control and treated plots prior to treatment, after the fourth and ninth applications, and at various intervals through 18 months following the last application at Plots A and C, and through 94 days following the last application at Plot B. Ten soil cores were collected from each plot at each sampling interval with a soil probe (diameter not specified). Samples were collected to a depth of 12 inches through October 21, 1986, and to a depth of 15 inches at later sampling intervals. Each soil sample was sectioned into 3-inch segments; segments from the same depth were composited, transferred into plastic bags, and frozen. The samples were then shipped frozen with dry ice to the analytical laboratory, where they were maintained frozen (temperature not reported) for an unspecified period of time prior to analysis.

The soil samples were thawed and mixed by hand. Subsamples (20 g) of the soil were extracted with acetone:10 N sulfuric acid (95:5, v:v) on a reciprocating shaker for 2 hours, then centrifuged.

Analysis for chlorothalonil by direct partitioning: An aliquot (equivalent to 5 g of soil) of the extract was mixed with additional acetone:10 N sulfuric acid (95:5, v:v) and water, and partitioned twice with petroleum ether by manual shaking for 2 minutes. The ether extracts from each partitioning were combined, mixed with keeper solution (2% paraffin oil in petroleum ether), concentrated in a water bath, and evaporated to dryness under a nitrogen stream. The resulting residues were dissolved in $MeCl_2$:hexane (20:80, v:v). Residues of chlorothalonil, and of hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN) (*described as manufacturing impurities of the test substance*) were selectively partitioned on a Florisil column. Chlorothalonil was eluted from the column with $MeCl_2$:hexane (20:80); HCB was eluted with $MeCl_2$:hexane:acetonitrile (50:48.5:1.5); PCBN was eluted with 0.05% acetonitrile in hexane:$MeCl_2$ (1:1, v:v). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. Resulting residues were dissolved in toluene and analyzed for chlorothalonil, HCB, and PCBN using GC with ^{63}Ni electron-capture detection. Method detection limits were 0.01 ppm for chlorothalonil, 0.003 ppm for HCB, and 0.005 ppm for PCBN.

Analysis for specific degradates by derivatization: An aliquot of the extract (equivalent to 10 g of soil) was transferred to a beaker and mixed with keeper solution and water. The acetone in the extract was evaporated. After the acetone was evaporated, a 0.4 M sodium carbonate solution was added, and the pH was adjusted to 4.5. The acidified extract was partitioned twice with petroleum ether by manual shaking for 2 minutes; both ether phases were discarded. The extracted aqueous phase was adjusted to pH <2, and sufficient sodium chloride was added to the solution to obtain a 30% solution (w:v). The solution was partitioned twice with water and diethyl ether by manual shaking for 2 minutes. The diethyl ether phases were combined and mixed with keeper solution, and the solution was concentrated in a water bath and evaporated to dryness under a nitrogen stream. The resulting residues were dissolved in acetone, and the resulting solution was divided into two equal portions. Each portion was concentrated and dried as described above.

One portion was used to derivatize the degradates 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701), 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525), and 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851) into their methyl ether and methyl ester derivatives.[1] Later (length of storage not specified), the derivatized sample was filtered through a glass chromatographic column. Derivatized SDS-3701 was eluted from the column with MeCl$_2$, and derivatized SDS-47525 and SDS-46851 were eluted with acetone:MeCl$_2$ (50:50). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The dried [^{14}C]residues were dissolved in toluene and quantified using GC with ^{63}Ni electron-capture detection. The method detection limits were 0.01 ppm for SDS-3701, and 0.03 ppm for SDS-46851 and SDS-47525.

The second portion was used for separation and cleanup of the degradates 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524) and 3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221). The dried residues were dissolved in MeCl$_2$; some portions were diluted with toluene and analyzed directly using GC with ^{63}Ni electron-capture detection. The remaining MeCl$_2$ solutions were filtered through a glass chromatographic column. The column was eluted with MeCl$_2$, which was discarded, followed by acetone:MeCl$_2$ (50:50). Keeper solution was added to each respective eluant, and the solutions were concentrated in a water bath, then dried under a nitrogen stream. The dried [^{14}C]residues were dissolved in toluene and quantified using GC with ^{63}Ni electron-capture detection. The method detection limits were 0.03 ppm for SDS-47523/24 and SDS-19221.[2]

DATA SUMMARY:

Chlorothalonil residues were variable in the upper 15 inches of sandy loam soil treated nine times at weekly intervals with chlorothalonil (Bravo 500, 4.17 lb/gal FlC) at 0.63 lb ai/A for a total of 5.7 lb ai/A. The two treated plots, which were previously planted to broccoli and located near Greenfield, California, were treated beginning August 13, 1986. Chlorothalonil was detected to a depth of 12-15 inches, the deepest layer sampled. Two degradates, 4-hydroxy-2,5,6-trichloro-isophthalonitrile (SDS-3701) and 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851) were detected to depths of 12-15 and 9-12 inches, respectively. In general, the degradates 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525), 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524) and 3-cyano-2,4,5,6-tetrachlorobenzamide

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[1] Concentrated HCL:methanol (1:3, v:v) and diazopropane solution were added to the dried residue, and the solution was allowed to sit in a fume hood at ambient temperature for 1 hour, after which the solvent was evaporated under a nitrogen stream. The residues were dissolved in MeCl$_2$ and refrigerated.

[2] To determine the validity of the method, fortified soil samples were analyzed. Recoveries from fortified soil samples were 67-133% for chlorothalonil, 67-116% for SDS-3701, 67-128% for SDS-47525, 62-138% for SDS-46851, 67-133% for SDS-19221, 67-133% for SDS-47523, 60-122% for HCB, and 67-152% for PCBN. Fortification levels were 0.03-15 ppm for chlorothalonil; 0.03-0.50 ppm for SDS-3701; 0.06-0.50 ppm for SDS-47525, SDS-46851, SDS-19221, and SDS-47523; 0.01-0.05 ppm for HCB; and 0.015-0.10 ppm for PCBN.

(SDS-19221) were not detected (<0.03 ppm) in any soil samples. The manufacturing impurity, pentachlorobenzonitrile (PCBN), was detected to a depth of 6 to 9 inches, hexachlorobenzene (HCB), also a manufacturing impurity, was not detected (<0.003 ppm) in any soil samples.

At one of the treated plots (Plot A), the average concentration of chlorothalonil in the 0- to 3-inch depth was 1.84 ppm after the fourth application and 2.21 ppm after the ninth application (Table 9). Following the ninth application, the average concentration of chlorothalonil decreased to 0.86 ppm at 7 days, increased to 1.27 ppm at 14 days, decreased to 0.36 ppm at 121 days, and varied from 0.01 to 0.10 ppm at 199 days to 18 months. At lower sampling depths, average concentrations of chlorothalonil were up to 0.50 ppm in the 3- to 6-inch depth, 0.23 ppm in the 6- to 9-inch depth, 0.44 ppm in the 9- to 12-inch depth, and 0.03 ppm in the 12- to 15-inch depth. Average concentrations of the degradate

4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701)

were a maximum of 0.34 ppm in the 0- to 3-inch depth at 62 days following the last application, 0.21 ppm in the 3- to 6-inch depth, 0.09 ppm in the 6- to 9-inch depth, 0.05 ppm in the 9- to 12-inch depth, and 0.02 ppm in the 12- to 15-inch depth. The degradate

3-carboxy-2,5,6-trichlorobenzamide (SDS-46851)

was a maximum of 0.08 ppm in the 0- to 3-inch depth, 0.09 ppm in the 3- to 6-inch depth, 0.04 ppm in the 6- to 9-inch depth, 0.03 ppm in the 9- to 12-inch depth, and was <0.03 ppm (not detected) in the 12- to 15-inch depth. The degradates

2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525),

3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524), and

3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221)

were not detected (<0.03 ppm) in any soil samples. The manufacturing impurity

pentachlorobenzonitrile (PCBN)

was detected to a depth of 9 to 12 inches and was a maximum of 0.030 ppm, and

hexachlorobenzene (HCB)

was not detected (<0.003 ppm).

At a second treated plot (Plot B), the average concentration of chlorothalonil in the 0- to 3-inch depth was 0.86 ppm after the fourth application and 1.25 ppm after the ninth application (Table 10). Following the ninth application, the average concentration of chlorothalonil decreased to 0.63 ppm at 7 days, increased to 2.29 ppm at 14 days, and decreased to 0.16 ppm by 94 days. At lower sampling depths, average concentrations of chlorothalonil were a maximum of 0.76 ppm in the 3- to 6-inch depth at 14 days following the last application, 0.21 ppm in the 6- to 9-inch depth, 0.40 ppm in the 9- to 12-inch depth, and 0.12 ppm in the 12- to 15-inch depth. Average concentrations of the degradate

4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) were a maximum of 0.26 ppm in the 0- to 3-inch depth at 62 days following the last application, 0.21 ppm in the 3- to 6-inch depth, 0.10 ppm in the 6- to 9-inch depth, 0.03 ppm in the 9- to 12-inch depth and 0.01 ppm in the 12- to 15-inch depth. The degradate

3-carboxy-2,5,6-trichlorobenzamide (SDS-46851)

was <0.03 ppm (not detected), except for at 94 days following the last application in the 6- to 9- and 9- to 12-inch depths at 0.06 ppm and 0.03 ppm, respectively. The manufacturing impurity

pentachlorobenzonitrile (PCBN)

was a maximum of 0.034 ppm in the upper 3 inches, and was detected to a depth of 9 to 12 inches at a maximum of 0.011 ppm.

Hexachlorobenzene (HCB)

was not detected (<0.003 ppm)

At Plot A, air temperatures ranged from 24 to 108 F and average daily soil temperatures (soil depth not specified) ranged from 42 to 70 F. At Plot B, air temperatures ranged from 29 to 86 F and average daily soil temperatures (soil depth not specified) ranged from 47 to 62 F. Precipitation totaled 8.16 inches at 410 days following the last application, and irrigation totaled 8.85 inches at 169 days following the last application. The slope of the field was 0 degrees and the depth to the water table was less than 100 feet.

COMMENTS:

1. The cultural practices employed during the course of the study compromised study results. The study protocol stated that after harvest of the primary crop (broccoli) "tillage of the soil is acceptable and recommended according to normal agricultural practices for the area and crop being planted". It was also stated that "all tillage operations should not disturb the soil at a depth exceeding 8 inches from the surface". At each of the treated plots, the broccoli crop was shredded and, as stated by the study author, "all chlorothalonil present on the foliage was transferred to the soil". The broccoli foliage was disked into the ground at Plot B but not at Plot A. The plots were disked 10-11 days after treatment. Both treated plots were subsequently chiseled to a depth of 14 inches; Plot A was chiseled on April 4, 1987, and Plot B was chiseled on October 28, 1986. It is highly probable that these practices (cultivation, disking, and chiseling) resulted in movement of chlorothalonil residues to lower soil depths.

   In addition to the atypical cultural practices employed during the study, study results may also have been compromised by soil sampling procedures used. A description of the technique, including sampling equipment used, was not provided; it was only stated that a soil sampling probe was used. The study author conceded that the presence of chlorothalonil at the 6- to 15-inch depths was likely due to tillage operations, adding that the sandy (loam) soil would be "quite susceptible to drag down of residues from upper levels by the sampling probe or mixing of levels when handling the probe". As stated by the study author, "because of these factors, it is not possible to clearly determine the soil mobility of chlorothalonil".

2. Soil was not sampled deeply enough to define the extent of leaching of chlorothalonil and its degradates. At both treated plots, chlorothalonil residues were detected in the 12- to 15-inch depth, the lowest soil depth sampled. At Plot A, concentrations of chlorothalonil and the degradate SDS-3701 in the 12- to 15-inch depth were up to 0.03 ppm and 0.02 ppm, respectively. At Plot B, chlorothalonil was detected at up to 0.12 ppm and SDS-3701 was detected at up to 0.03 ppm in the 12- to 15-inch depth. The soil should have been sampled to depths (preferably two sampling depths) at which residues were nondetectable.

3. The length of freezer storage time, storage temperature of soil samples stored prior to analysis, and freezer storage stability data were not provided. Freezer storage stability data should be provided for the longest period of freezer storage.

4. A complete description of the soil sampling procedures was not provided. A description of the soil probe used to collect the soil samples, including type and diameter, was not reported.

5. Field data, including meteorological data, were incomplete. Meteorological data were provided beginning October 10, 1986, although the study was initiated on August 13, 1986. Soil temperature data were given as daily averages, rather than as maximum and minimum temperatures; the depth at which soil temperatures were recorded was not specified. For intervals for which both were provided, the precipitation data for the Greenfield weather station conflicted with that for the actual field site. Therefore, the precipitation totals reported in the data summary were obtained from the field records only. Both the precipitation and irrigation data were incomplete; precipitation data were only for August 13, 1986 through November 21, 1987, and irrigation data were only for August 13, 1987 through March 23, 1987. In addition, irrigation data in the field records were partially illegible and difficult to decipher. It was not stated whether there was subsurface drainage.

6. The data summarized in this review were obtained from Summary Tables 9-11 of the original document and are the mean residues of the major compounds found in the soil samples.

7. The study author calculated a half-life of 40 days for chlorothalonil using residue data from the upper 12 inches of soil at Plots A and B. However, because of the inherent problems associated with this study (atypical cultural practices and possible problems with the soil sampling technique), an accurate half-life determination for chlorothalonil cannot be made using these data. In addition, the author stated that the residue data from days 0 and 7 were not used due to the confounding effects of the cultural practices employed early in the study. The arbitrary exclusion of data used to calculate the half-life causes the resulting half-life to be of questionable value.

8. Residues of chlorothalonil, its degradates, and manufacturing impurities of the test substance (HCB and PCBN) were not detected in any control soil samples or in pretreatment samples taken from the two treated plots (Table 9-11).

9. The pesticide and crop history at the test site prior to the initiation of the study was not reported. Cultural maintenance practices employed during the study included cultivation, weeding, disking, and chiseling. During the study period, the plots were treated with Dacthal at 5 lbs/A, Lorsban at 7 lbs/A, and fertilizer (0-20-0) at 30 gals on July 11, 1986; Lorsban at 6 lbs/A on November 10, 1986; and Diazinon AG 500 at 1 pt/A on July 17, 1987.

10. Plot B was replanted to broccoli on April 28, 1987, and re-treated with ten additional applications of Bravo 500 at 2.5 pints/A (total 25.0 pints/A), made at 7-day intervals, beginning January 19, 1987. These second-year applications were part of a rotational crop study and not part of the soil dissipation study. The data for the rotational crop portion of this study are provided in separate documents, and are reviewed in Study 4 of this report.

11. The original document was poorly organized and required extensive perusal on the part of the reviewer to obtain the pertinent information for review of the study. The methodology for the experiment was incomplete and was scattered throughout the 360-page document. Much of the information was reported in handwritten field records included in the original document; these records were partially illegible and difficult to decipher. The registrant should have presented the details of the study in a more organized manner, so that the pertinent information could be readily obtained from the document.

CHLOROTHALONIL Sh# 081901

Page_____ is not included in this copy.

Pages 64 through 74 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.

X 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.

DATA EVALUATION RECORD

STUDY 4

CHEM 081901 Chlorothalonil 162-1

FORMULATION--14--FLOWABLE CONCENTRATE

STUDY ID 41564832 -- Rose, C.A. and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated root and bulb crops from Bravo treated areas - 1987. Doc. No. 1401-86-0084-CR-009. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564833 -- Rose, C.A. and D.L. Ballee. 1990. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated root and bulb crops from Bravo treated areas - 1987. Addendum I - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-009-001. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564834 -- King, C., P.M. Prince, and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated oil bearing/bean crops from Bravo treated areas - 1986, 1987. Doc. No. 1401-86-0084-CR-005. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564835 -- King, C., P.M. Prince, and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated oil bearing/bean crops from Bravo treated areas - 1986, 1987. Addendum I - peanut hay, bean hay and pea fodder. Doc. No. 1401-86-0084-CR-005-001. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564836 -- King, C., P.M. Prince, and D.L. Ballee. 1990. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated oil bearing/bean crops from Bravo treated areas - 1986, 1987. Addendum II - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-005-002. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564837 -- King, C., P.M. Prince, and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated oil bearing/bean crops from Bravo treated areas - 1986, 1987. Report amendment number three. Doc. No. 1401-86-0084-CR-005-003. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564838 -- Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated leafy crops from Bravo treated areas - 1985-1987. Doc. No. 1401-86-0084-CR-010. Unpublished study performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564839 -- Kenyon, R.G. and D.L. Ballee. 1990. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated leafy crops from Bravo treated areas - 1985-1987. Addendum I - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-010-001. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564840 -- Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated leafy crops from Bravo treated areas - 1985-1987. Doc. No. 1401-86-0084-CR-010-002. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564841 -- Wiedmann J.L. and D.L. Ballee. 1990. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated fruiting vegetables and cucurbits from Bravo treated areas - 1985-1987. Doc. No. 1401-86-0084-CR-011. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564842 -- Wiedmann J.L. and D.L. Ballee. 1990. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated fruiting vegetables and cucurbits from Bravo treated areas - 1986-1987. Addendum I - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-011-001. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564843 -- Rose, C.A. and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated grain crops from Bravo treated areas - 1987. Doc. No. 1401-86-0084-CR-006. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564844 -- Rose, C.A. and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated grain crops from Bravo treated areas - 1987. Addendum I - straw and forage. Doc. No. 1401-86-0084-CR-006-001. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564845 -- Rose, C.A. and D.L. Ballee. 1989. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated grain crops from Bravo treated areas - 1987. Report amendment. Doc. No. 1401-86-0084-CR-006-002. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564846 -- Rose, C.A. and D.L. Ballee. 1990. Rotational crop study: Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB and PCBN on rotated grain crops from Bravo treated areas - 1987. Addendum II - soil at planting and harvesting of crops. Doc. No. 1401-86-0084-CR-006-003. Unpublished, performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH; submitted by Fermenta ASC Corporation, Mentor, OH.

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CONCLUSIONS:

Field Accumulation - Rotational Crops

1. This study cannot be used to fulfill data requirements at this time. It is unacceptable at present for the following reason:

   The data were not presented in a reviewable format, and therefore levels of chlorothalonil and its degradates in the soil immediately posttreatment and at planting and harvest of the rotational crops could not be adequately assessed.

4. In order for this study to be reevaluated, the registrant must provide summarized soil residue data, complete site characteristics, and meteorological data. In addition, the lengths of time the samples were stored frozen and acceptable freezer storage stability data must be provided.

METHODOLOGY:

Chlorothalonil (Bravo 500 and 720; 4.17 and 6.0 lb/gallon FlC, respectively) was broadcast sprayed at 1-2 lb ai/A/-application (1.5-4.0 pints/A/application) three

77

356

to twelve times at 7- to 20-day intervals to field plots of varying sizes and soil types located at twelve sites in nine states (Summary Tables 1 and 2). At each site, one or two plots were treated and an additional untreated plot was maintained as a control. The plots were planted to various primary crops prior to treatment, which were then harvested at normal maturity. At plant-back intervals ranging from 13 to 284 days posttreatment, various leafy vegetable, root/bulb, grain, oil bearing/bean, and/or fruiting vegetable/cucurbit rotational crops were planted in the treated and control plots. All crops were harvested at maturity. Soil cores (diameter unspecified, 0- to 12- or 0- to 15-inch depths) were taken prior to treatment, following the final application (Fresno, CA; Greenfield/Watsonville, CA; and Donalsonville, GA sites only), when the crops were planted, and at mature crop harvests. Plant and soil samples were stored frozen for unspecified lengths of time until analysis.

Leafy vegetable (lettuce, spinach, cabbage, collards, celery, and broccoli), root/bulb (carrot, beet, and turnip tops and roots; radish roots; potatoes; sweet potatoes; and onions), straw/forage (wheat, oat, and sorghum), hay/fodder (peanut, bean, and pea), and fruiting vegetable/cucurbit (tomatoes, bell peppers, cantaloupe, cucumbers, and summer and winter squash) samples were chopped or ground, then duplicate subsamples (20-100 g) were extracted with acetone:10 N sulfuric acid (95:5) and filtered (for tomatoes, the entire 200-600 g sample was extracted). An aliquot of the filtrate was removed, diluted with water (root/bulb, straw/forage, and hay/fodder samples), and partitioned twice with petroleum ether. Ether phases were combined, treated with 2% paraffin oil in petroleum ether, then reduced to dryness. The residue was redissolved in hexane:methylene chloride (80:20). For leafy vegetable, root/bulb, and fruiting vegetable/cucurbit samples, two aliquots of the residue were applied to separate Florisil columns. Chlorothalonil was eluted from one of the columns with methylene chloride:hexane:acetonitrile (50:48.5:1.5). Hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN) were eluted from the second column with hexane:methylene chloride (80:20) and hexane:methylene chloride:acetonitrile (50:50:0.05), respectively. For straw/forage and hay/fodder samples, a single Florisil column was used; HCB was eluted with hexane:methylene chloride (80:20), then chlorothalonil and PCBN were co-eluted with methylene chloride:hexane:acetonitrile (50:48.5:1.5).

To extract 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) and 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851), an additional aliquot of the acetone:sulfuric acid filtrate was diluted with water (leafy vegetable, root/bulb, and fruiting vegetable/cucurbit samples), and the acetone was removed by evaporation. A solution of 0.4-1.0 M sodium bicarbonate was added, the pH was adjusted to 4.5, and then the solution was partitioned twice with petroleum ether (leafy vegetable, root/bulb, and fruiting vegetable/cucurbit samples) or 1:1 ethyl ether:petroleum ether (straw/forage and hay/fodder samples); petroleum ether phases were discarded. The aqueous phase was adjusted to pH <1-2, combined with sodium chloride (30%, w:v), and partitioned twice with diethyl ether. Ether extracts were combined and concentrated, and SDS-3701 was converted to its methyl ether derivative and SDS-46851 to its methyl ester derivative using concentrated hydrochloric acid:methanol (1:3) and diazomethane solution. The derivatized solution was concentrated, redissolved in methylene chloride, and applied to an alumina column. Methyl SDS-3701 was eluted with methylene chloride, and methyl SDS-46851 was eluted with acetone:methylene chloride (50:50). For straw/forage and hay/fodder samples, the eluant containing methyl SDS-46851 was applied to a silica Sep-Pak column and eluted with petroleum ether:ethyl acetate (65:35).

To isolate chlorothalonil, HCB, and PCBN from grain (wheat, corn, sorghum, oats, and rice) and some oil bearing/bean crops (peanut nutmeats and hulls, soybean seed, dry beans, dry peas, rapeseed and cottonseed), samples were ground, then duplicate subsamples (20-100 g) were extracted with acetonitrile and filtered. An aliquot of the filtrate was diluted with water, combined with 10 N sulfuric acid, then partitioned twice with petroleum ether. Ether extracts were combined, concentrated, and cleaned up using Florisil column chromatography as described above for leafy vegetables. To isolate SDS-3701 and SDS-46851 from grain, additional subsamples were extracted with acetone:10 N sulfuric acid (95:5), partitioned, derivatized, and cleaned up using alumina column chromatography as described above. To isolate SDS-3701 and SDS-46851 from the oil bearing/bean crops, additional subsamples were extracted with acetone:10 N sulfuric acid (95:5) and filtered. Acetone was evaporated from an aliquot of the filtrate, the pH was adjusted to <2, sodium chloride was added, and the sample was partitioned twice with diethyl ether. Ether extracts were combined, concentrated, derivatized, and cleaned up using alumina column chromatography as described above.

Chlorothalonil, HCB, and PCBN were extracted from fresh pea samples (50 g) as described above for leafy vegetables. To extract SDS-3701 and SDS-46851, an additional aliquot of the acetone:sulfuric acid filtrate was combined with water, then prepared and extracted as described above for the oil bearing/bean crops.

Lima beans (100 g) were extracted with acetone:10 N sulfuric acid (95:5) and filtered. An aliquot of the filtrate was combined with water and 2% paraffin oil in petroleum ether, then acetone was removed by evaporation. Sodium bicarbonate solution (0.4 M) was added, the pH was adjusted to 4.5, then the solution was partitioned twice with petroleum ether. To isolate chlorothalonil, HCB, and PCBN, ether extracts were combined, concentrated, and cleaned up using Florisil column chromatography as described above for leafy vegetables. To isolate SDS-3701 and SDS-46851, the pH of the remaining aqueous phase was reduced to <2, sodium chloride was added, and the sample was partitioned twice with diethyl ether. Ether extracts were combined, concentrated, derivatized, and cleaned up using alumina column chromatography as described above.

All eluants were treated with 2% paraffin oil in petroleum ether, evaporated to dryness, redissolved in toluene, and analyzed using GC with electron-capture detection. The detection limits were 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. Recovery efficiencies from fortified plant samples ranged from approximately 60 to 130% of the applied for chlorothalonil, SDS-3701, and PCBN; 60 to 140% for HCB; and 60 to 160% for SDS-46851 (Tables 1-A through 1-G).

Soil cores were divided into 3-inch segments, composited by depth and sampling interval, and thoroughly mixed. Duplicate subsamples (20-40 g) were extracted with acetone:10 N sulfuric acid (95:5) for 2 hours, then centrifuged. Chlorothalonil, HCB, and PCBN were extracted from an aliquot of the supernatant and isolated using Florisil column chromatography as described above for leafy vegetables. As an alternate method of isolation, an additional aliquot of the residue dissolved in hexane:methylene chloride was applied to a Florisil column, then HCB was eluted with hexane:methylene chloride (80:20) and PCBN plus chlorothalonil were eluted with methylene chloride:hexane:acetonitrile (50:48.5:1.5). An additional aliquot of the supernatant was combined with 2% paraffin oil in petroleum ether and water (50:5:10), acetone was removed by evaporation, then SDS-3701, SDS-46851, and 2,4,5-trichloro-3-cyano-6-hydroxybenzamide (SDS-47525) were extracted, derivatized, and isolated using alumina column chromatography as described above for leafy vegetables; SDS-47525 co-eluted with SDS-46851. 3-Cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221) and the isomers of 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524) were co-extracted from the supernatant along with SDS-3701, SDS-46851, and SDS-47525, but were not derivatized; an aliquot of the ether residue was dissolved in methylene chloride, applied to an alumina column, then SDS-47523/SDS-47524 and SDS-19221 were co-eluted with acetone:methylene chloride (50:50). All eluants were prepared and analyzed using GC as described above. The detection limits were 0.01 ppm for chlorothalonil and SDS-3701; 0.03 ppm for SDS-46851, SDS-47525, SDS-47523/SDS-47524, and SDS-19221; 0.003 ppm for HCB; and 0.005 ppm for PCBN. Recovery efficiencies from soil samples fortified with chlorothalonil and its degradates ranged from approximately 60 to 150% of the applied (Tables 2-A through 2-E).

DATA SUMMARY:

In general, chlorothalonil residues did not appear to accumulate in mature leafy vegetable (lettuce, spinach, cabbage, collards, celery, and broccoli), root/bulb (carrots, beets, turnips, radishes, potatoes, sweet potatoes, and onions), grain (wheat, oats, sorghum, corn, and rice), oil bearing/bean (peanuts, soybean, cotton, rape, peas, beans, and lima beans), and fruiting vegetable/cucurbit (tomatoes, bell peppers, cantaloupe, cucumbers, and summer and winter squash) crops planted at intervals ranging from 13 to 248 days after 3 to 12 applications at 7- to 20-day intervals of chlorothalonil (Bravo 500 and 720; 4.17 and 6.0 lb/gallon FlC, respectively) at 1-2 lb ai/A/application to field plots located throughout nine states. The major degradate detected in the crops was

3-carboxy-2,5,6-trichlorobenzamide (SDS-46851).

There was no apparent correlation between the levels of SDS-46851 detected in the crops and the treatment-to-planting intervals. Minor degradates included

4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701),

hexachlorobenzene (HCB), and

pentachlorobenzonitrile (PCBN),

which were only detected in a few isolated samples and did not significantly exceed the detection limits of the compounds in the various plant matrices.

Chlorothalonil at harvest was $\leq$0.02 ppm in collards and was not detected (<0.01 ppm) in lettuce, spinach, celery, broccoli, and cabbage (Table 3-A). SDS-46851 was detected at 0.11-0.19 ppm in broccoli and at up to 0.80 ppm in spinach, but was not detected (<0.03 ppm) in lettuce, celery, cabbage, and collards. SDS-3701 was $\leq$0.02 ppm in lettuce, $\leq$0.01 ppm in spinach, and was not detected (<0.01 ppm) in celery, broccoli, cabbage, and collards. PCBN was ≤0.008 ppm in cabbage and was not detected (<0.005 ppm) in any other leafy crop; HCB was not detected (<0.003 ppm) in any leafy crop.

Except for sugar beet roots from the ND site, chlorothalonil at harvest was ≤0.02 ppm in red/table and sugar beets (tops and roots), carrots (tops and roots), turnips (tops and roots), radishes (roots only), potatoes, sweet potatoes, and onions (Tables 3-A and 3-B). One sample of sugar beet root from the ND site (treatment-to-planting interval not provided) contained 0.05 ppm chlorothalonil, but chlorothalonil was not detected in the corresponding duplicate sample. SDS-46851 was detected at 0.32-0.33 ppm and 0.20-0.21 ppm in red/table beet tops and roots, respectively; at up to 0.07 ppm and up to 0.14 ppm in sugar beet tops and roots; at up to 0.39 ppm and up to 0.24 ppm in carrot tops and roots; at 0.45-0.60 ppm and 0.09-0.11 ppm in turnip tops and roots; at 0.10 ppm in radish roots; at up to 0.67 ppm in potatoes; at ≤0.03 ppm in onions; and was not detected in sweet potatoes. SDS-3701 was ≤0.02 ppm in carrot roots and tops, ≤0.01 ppm in turnip tops and potatoes, and was not detected in turnip roots, red/table and sugar beets (tops and roots), radish roots, sweet potatoes, and onions. HCB and PCBN were detected at 0.006 and 0.005 ppm, respectively, in carrot roots from the Fresno, CA site, but were not detected in any other root/bulb crop from that site or any other site.

Chlorothalonil was ≤0.03 ppm in mature sorghum grain, ≤0.01 ppm and ≤0.02 ppm in wheat grain and straw, and was not detected in sorghum forage, oat grain and straw, corn grain, and rice grain (Tables 3-C and 3-D). In immature wheat forage harvested at 146 days postplanting (Fresno, CA site), chlorothalonil was 0.01 ppm. SDS-46851 was detected at 0.07-0.08 ppm in immature wheat forage, at up to 0.26 ppm in wheat grain and straw, at 0.39-0.40 and 2.88-3.02 ppm in oat grain and straw, at up to 0.14 ppm in corn grain, at 0.24-0.27 ppm in sorghum forage, and was not detected in sorghum grain and rice grain. SDS-3701 was detected at 0.04 ppm in sorghum forage, at up to 0.04 ppm in wheat straw, at ≤0.02 ppm in oat straw, and was not detected in wheat forage and wheat, corn, sorghum, oat, and rice grain. In all grain and straw/forage samples, PCBN was ≤0.005 ppm, and HCB was not detected.

Except for cottonseed from the Fresno, CA site and peanut hulls from the OK site, chlorothalonil was not detected at harvest in peanut nutmeats, soybean seed, cottonseed, rapeseed, fresh and dry peas, dry beans, and lima beans (Table 3-E). Chlorothalonil was 0.02-0.03 ppm in cottonseed from the Fresno, CA site (planted at 177 days posttreatment) and 0.01-0.02 ppm in peanut hulls from the OK site (planted at 263 days). Chlorothalonil was detected at 0.20-0.24 ppm in peanut hay (Donalsonville, GA site; treatment-to-planting interval not provided), 0.08-0.1 ppm in bean hay (ID, planted at 269 days), and 0.05-0.06 ppm in pea fodder (ID, planted at 249 days); however, the study authors reported that the residues appear to be the result of spray drift contamination. SDS-46851 was detected at 0.08 ppm in fresh peas, 0.10-0.11 ppm in bean hay, up to 0.11 ppm in soybean seed, and up to 0.05 ppm in cottonseed. SDS-46851 was not detected in peanut nutmeats, hulls, and hay; rapeseed; dry peas and fodder; dry beans; and lima beans. SDS-3701 was detected at 0.07 ppm in pea fodder, but was ≤0.02 ppm in peanut nutmeats, hulls, and hay; soybean seed; cottonseed; rapeseed; fresh and dry peas; dry beans and hay; and lima beans. HCB and PCBN were not detected in any oil bearing/bean crop.

Chlorothalonil at harvest was ≤0.02 ppm in tomatoes, bell peppers, cantaloupe, cucumbers, and winter squash (Table 3-F). One sample of summer squash from the

Donalsonville, GA site (planted at 222 days posttreatment) contained 0.04 ppm chlorothalonil, but chlorothalonil was not detected in the corresponding duplicate sample. SDS-46851 was detected at 0.94-1.15 ppm in winter squash, up to 0.15 ppm in cucumbers, up to 0.07 ppm in tomatoes, and was not detected in bell peppers, cantaloupe, and summer squash. SDS-3701 was $\leq$0.01 ppm in summer squash and was not detected in tomatoes, bell peppers, cantaloupe, cucumbers, and winter squash. HCB and PCBN were not detected in any fruiting vegetable/cucurbit crop.

Levels of chlorothalonil and its degradates in the soil immediately posttreatment and at planting and harvest of the rotational crops could not be adequately assessed because the data were not presented in a reviewable format.

COMMENTS:

1. Data from analysis of soil samples taken at planting and harvest of the rotational crops were provided, but were not reviewed because the data were not summarized and were not presented in a readily reviewable format. Soil residue data should be summarized according to site and be presented in chronological order indicating planting and harvest dates of the rotational crops or treatment-to-planting intervals and treatment-to-harvest intervals. In these documents (MRIDs 415648-33, -36, -39, -42, and -46), a separate soil residue table was presented for the planting of each crop and the harvest of each crop at each test site making it impossible to adequately review the dissipation of the pesticide in the field plots without extensive summarization by the reviewer.

2. It appeared that immediate posttreatment soil samples were taken at only three of the test sites (Fresno, CA; Greenfield, CA; and Donalsonville, GA). These data were not supplied with the documents concerning the rotational crop studies, but were contained in the documents concerning the terrestrial field dissipation studies (MRIDs 41564828-30). Although the data were available, they were not reviewed (see Comment 1). It could not be determined if immediate posttreatment soil samples were taken at the remaining test sites. Data from analysis of immediate posttreatment soil samples from the various test sites must be provided to demonstrate that the application rates were confirmed.

3. The investigator did not report how long plant and soil samples were stored frozen prior to analysis.

4. Adequate freezer storage stability were not provided for the crop and soil substrates. Storage stability data were not provided for lettuce, spinach, cabbage, collards, broccoli, beets, turnips, radishes, sweet potatoes, onions, wheat straw, oat grain and straw, sorghum grain and forage, corn grain, rice grain, peanuts, cottonseed, rapeseed, peas, beans, and lima beans, bell peppers, cantaloupe, summer and winter squash, and soil. Storage stability studies concerning chlorothalonil residues in carrot roots, potatoes, celery, soybeans, tomatoes, cucumbers, cherries, and wheat grain (Study 5, MRIDs 41564820-27) were conducted, but were found to be unacceptable because of an inappropriate experimental design.

5. Treatment-to-planting intervals presented by the registrant in the rotational crop residue tables (designated PPI in the document tables) were often incomplete or incorrect (compare with Summary Table 2). The reviewer determined treatment-to-

planting intervals from final application and planting dates presented in MRIDs 415648-33, -36, -39, -42, and -46. Treatment-to-planting intervals were not provided for all rotational crops from the Donalsonville, GA and Grand Forks, ND sites. Treatment-to-harvest intervals (designated PHI in the document tables) presented by the registrant were accurate.

6. Meteorological data (primarily precipitation and temperature) were submitted by the registrant as unsummarized field records. These data should be summarized upon resubmission of these documents.

7. The test soils from the Parrot, GA; Plains, GA; ID; MD; NY; ND; and OK sites were not completely characterized (See Summary Table 1). Site characteristics, including soil type, soil characterization, and plot size, were not summarized by the registrant. This information was compiled by the reviewer and may be incomplete due to the voluminous nature of the field records. Site characteristics were incomplete; depth to the water table and slope of the field were not provided for all test sites. Field maintenance practices were provided for some of the sites; however, because the study is unacceptable and there is a large volume of information concerning field maintenance practices, the reviewer did not extract the pertinent information.

8. Field test methodology was not adequately described: although the number of chlorothalonil applications to each site were reported, dates of application had to be obtained from the field records; sampling procedures for the crops, such as number of samples per plot and size of samples, were not described; and sampling procedures for the soil, such as core diameter and number of cores/plot/sampling interval, were not described.

9. Application rates were provided in terms of lb ai/A for only six of the test sites (obtained from MRID 41564831) and are as follows: Fresno, CA - 2.09 lb ai/A; Greenfield, CA - 1.17 lb ai/A; Donalsonville, GA - 1.13 lb ai/A; Grand Forks, ND - 1.04 lb ai/A; Eakly, OK -1.13 lb ai/A; and Donna, TX - 2.25 lb ai/A. Application rates for Parrot, GA; Plains, GA; Minidoka, ID; Rosa, LA; Salisbury, MD; and Phelps, NY, were only provided in terms of pint formulation/A. Due to the number of sites involved, the reviewer did not convert data for all sites from pints/A to lbs ai/A; however, based on all values for pints/A/application and lb/gal of formulation, the reviewer did determine that the range of single applications is 1-2 lb ai/A/application.

10. Except for wheat forage at the Fresno, CA site, immature plants were not analyzed.

11. Except for three plant samples (peanut hay, bean hay, and pea fodder) chlorothalonil did not appear to accumulate in any rotational crop. Chlorothalonil was detected at 0.20-0.24 ppm in the peanut hay (Donalsonville, GA site; no treatment-to-planting interval), 0.08-0.1 ppm in the bean hay (ID, planted at 269 days), and 0.05-0.06 ppm in the pea fodder (ID, planted at 249 days). The study authors reported that the residues appear to be the result of spray drift contamination. Dry beans and peas were collected with the hay and fodder at the ID site and did not contain any chlorothalonil. Only peanut hay was analyzed at the Donalsonville, GA site, and it was not determined if there was chlorothalonil uptake by any other part of the peanut plants.

Summary Table 1. Soil and site characterization.[a]

		%						
Location	Classification	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)	Plot size
Fresno, CA	Sandy loam	58	32	10	0.4	6.6	5.3	60 x 90 feet
Greenfield/ Watsonville, CA	Sandy loam	68.4	29.2	2.4	0.21	6.6	14	0.5 acre
Donalsonville, GA	Sandy loam	70	15	15	2.1	5.3	2.4	36 x 100 feet
Parrot, GA	Loamy sand	--[b]	--	--	--	--	--	--
Plains, GA	--	--	--	--	--	--	--	--
Minidoka, ID	Silt loam	15	65	20	1.4	7.9	--	45 x 320 feet
Rosa, LA	Sandy loam	52	45	3	0.8	7.0	4.7	51 x 132 feet
Salisbury, MD	Sandy loam	--	--	--	--	6.2	--	45 x 112 feet
Phelps, NY	Sandy loam	80.8	4.4	14.8	1.9	6.0	--	50 x 120 feet
Grand Forks, ND	--	--	--	--	--	--	--	--
Eakly, OK	Sand	87.5	9	3.5	0.5	--	--	50 x 120 feet
Donna, TX	Sandy clay loam	59	17	24	1.2	8.0	15.8	90 x 107 feet

[a] Information compiled by reviewer from field records provided in MRIDs 415648-32, -34, -38, -41, and -43.

[b] Not available.

Summary Table 2. Field trial specifics.[a]

Location	Formulation	Rate (pint/A)	Number of applications	Dates of application	Primary crop treated	Rotational crop	Treatment-to-planting interval (days)[b]	Treatment-to-planting interval (days)[c]
Fresno, CA	Bravo 500	4.0	8	08/26/86-10/14/86	Tomato	Lettuce	31	163
						Broccoli	31	185
						Carrots[d]	31	185
						Sugarbeets	31	290
						Onions	31	224
						Wheat forage	31	177
						Wheat[e]	31	224
						Cottonseed	177	360
						Tomatoes	177	318
Greenfield/ Watsonville, CA	Bravo 500	2.25	9	08/13/86-10/07/86	Broccoli	Spinach	197	248
						Lettuce	197	290
						Broccoli	197	290
						Celery	197	413
						Radishes	197	238
						Potatoes	197	302
						Carrots (roots only)	197	309
						Sugarbeets (roots only)	197	363
						Wheat	197	314
						Peas-fresh	223	297
						Peas-dried	223	309
Donalson-ville, GA	Bravo 720	1.5	10	06/20/86-09/18/86	Peanut	Cabbage	34	180
						Turnip tops	34	60
						Turnip roots	34	91
						Sweet potatoes	222	390
						Wheat	34	253
						Corn grain	180	320
						Peanut hay	--[f]	378
						Soybeans	253	414
						Cottonseed	253	414
						Summer squash	222	291
Parrot, GA	Bravo 500	2.125	11	05/28/85-09/14/85	Peanut	Wheat	83	270
						Corn grain	208	328
						Sorghum grain	240	328
Plains, GA	Bravo 500	2.125	6	06/01/85-08/14/85	Peanut	Collards	204	286
						Wheat	90	279
						Corn grain	214	351
						Sorghum grain	280	392
						Cottonseed	280	429

(Continued)

Summary Table 2. (Continued)

Location	Formulation	Rate (pint/A)	Number of applications	Dates of application	Primary crop treated	Rotational crop	Treatment-to-planting interval (days)^b	Treatment-to-planting interval (days)^c
Minidoka, ID	Bravo 720	1.5	8	07/18/86 09/05/86	Potato	Sugarbeets	221	374
						Carrots	249	344
						Potatoes	245	376
						Wheat	221	370
						Peas-dried and fodder	249	351
						Rapeseed	249	370
						Beans-dried and hay	269	374
Rosa, LA	Bravo 720	2.0	3	08/20/86- 09/25/86	Soybean	Rice grain	194	322
Salisbury, MD	Bravo 720	3.0	8	07/11/86- 08/29/86	Tomato	Carrots	284	402
						Table (red) beets	284	402
						Turnips (tops only)	284	420
						Wheat (grain only)	32	300
						Corn grain	284	412
						Lima beans	283	381
						Soybeans	283	420
						Tomatoes	272	381
						Cantaloupes	283	341
Phelps, NY	Bravo 500	2.125	12	08/02/86- 10/18/86	Potato	Spinach	229	320
						Cabbage	229	320
						Carrots	229	320
						Potatoes	236	362
						Onions	229	391
						Corn grain	199	348
						Oats	178	282
						Soybeans	229	362
						Tomatoes	229	327
						Winter squash	229	341
Grand Forks, ND	Bravo 500	2.0	8	07/18/86- 09/15/86	Potato	Lettuce	257	316
						Cabbage	--	350
						Potatoes	--	350
						Sugarbeets	--	385
						Wheat	--	333
						Soybeans	259	385

(Continued)

86

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Summary Table 2. (Continued)

Location	Formulation	Rate (pint/A)	Number of applications	Dates of application	Primary crop treated	Rotational crop	Treatment-to-planting interval (days)[b]	Treatment-to-planting interval (days)[c]
Eakly, OK	Bravo 720	1.5	8	07/14/86-10/06/86	Peanut	Potatoes	179	282
						Wheat	59	260
						Corn grain	220	290
						Sorghum grain	260	380
						Peanuts	263	380
						Peanut hulls	263	380
						Cottonseed	263	422
						Cucumbers	262	330
Donna, TX	Bravo 720	3.0	8	09/19/86-11/06/86	Cucumber	Spinach	13	100
						Carrots	13	175
						Onions	13	175
						Sorghum grain and forage	99	228
						Cottonseed	99	277
						Cucumbers	99	190
						Bell peppers	99	228

[a] Information compiled by reviewer.

[b] Intervals determined from final application and planting dates presented in MRIDs 415648-33, -36, -39, -42, and -46.

[c] Described as "PHI" in study documents.

[d] Except where indicated, tops and roots were collected at harvest of carrots, beets, and turnips.

[e] Except for the MD site, grain and straw were collected at harvest of wheat and oats.

[f] Not available.

CHLOROTHALONIL Sh# 081901

Page_____ is not included in this copy.

Pages 88 through 114 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.

DATA EVALUATION RECORD

STUDY 5

CHEM 081901 Chlorothalonil 162-1

FORMULATION--14--FLOWABLE CONCENTRATE

STUDY ID 41564820 -- Rose, C., K.A. Dillon, and D.L. Ballee. 1990. Residues of tetrachloroiso-phthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in carrots from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0096-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564821 -- Rose, C., K.A. Dillon, and D.L. Ballee. 1990. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in potatoes from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0095-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564822 -- King, C., J.L. Wiedmann, and D.L. Ballee. 1990. Residues of tetrachloro-isophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in celery from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0136-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564823 -- Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1990. Residues of tetra-chloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in soybeans from a stability study (field incurred)--1988-- 1-year interim report. Doc. No. 3064-88-0097-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564824 -- Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1990. Residues of tetra-chloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in tomatoes from a stability study (field incurred)--1988-- 1-year interim report. Doc. No. 3064-88-0083-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564825 -- Wiedmann, J.L. and D.L. Ballee. 1990. Residues of tetrachloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in cucumbers from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0093-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564826 -- King, C., J.L. Wiedmann, and D.L. Ballee. 1990. Residues of tetrachloro-isophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in cherries from a stability study (field incurred)--1988--1-year interim report. Doc. No. 3064-88-0068-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO, and submitted by Fermenta ASC Corporation, Mentor, OH.

STUDY ID 41564827 -- Kenyon, R.G., J.L. Wiedmann, and D.L. Ballee. 1990. Residues of tetra-chloroisophthalonitrile (chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN in wheat grain from a stability study (field incurred) --1988--1-year interim report. Doc. No. 3064-88-0070-CR-001. Performed by Department of Environmental Sciences, Ricerca, Inc., Painesville, OH, and Stewart Agricultural Research Services, Inc., Macon, MO; and submitted by Fermenta ASC Corporation, Mentor, OH.

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CONCLUSIONS:

Ancillary Study - Freezer Storage Stability

1. This study cannot be used to fulfill data requirements. The deficiencies cannot be resolved with the submission of additional data. A new study must be conducted.These data are considered to be of uncertain value and should not be used to predict the environmental behavior of chlorothalonil and its degradates.

2. This study is unacceptable for the following reason:

   the experimental design was not appropriate for determining freezer storage stability of chlorothalonil and its degradates in these plant matrices.

METHODOLOGY:

Chlorothalonil (Bravo 720, 6.0 lb/gallon FlC) was broadcast sprayed at 2.25-15 lb ai/A/application (3-20 pints formulation/A/application) four to sixteen times at 3- to 16-day intervals to field plots of varying sizes and soil types located at six sites in four states (Summary Table 1). One crop (carrots, potatoes, celery, soybeans, tomatoes, cucumbers, cherries, or wheat) was planted at each site. An untreated plot planted to the respective crop was maintained as a control at each site. Approximately 50 samples of mature carrots (2 lb/sample), potatoes (eight tubers/sample), celery (twelve quarters/sample), soybeans (2 lb/sample), cucumbers (five to eight/sample), cherries (1 lb/sample), and wheat grain (2 lb/sample), and 150 samples of tomatoes (three to four/sample) were harvested immediately after the final application of chlorothalonil. Upon harvest of each treated crop, two samples (carrots, potatoes, celery, soybeans, cucumbers, cherries, and wheat grain) or four samples (tomatoes) were processed immediately for analysis. The remaining samples of each crop were analyzed for chlorothalonil and its degradates after approximately 1 day, 1 week, and 1, 3, 6, 9, and 12 months of frozen (-10 to 20 F) storage.

Carrots (roots only), potatoes, celery, and cucumbers were chopped prior to analysis; tomatoes were left intact. Duplicate subsamples (50-100 g of carrots, potatoes, and celery; 3-4 whole tomatoes) were extracted with acetone:10 N sulfuric acid (95:5) and filtered. An aliquot of the filtrate was removed, diluted with water (carrots and potatoes), and partitioned twice with petroleum ether. Ether phases were combined, treated with 2% paraffin oil in petroleum ether, then reduced to dryness. The residue was redissolved in hexane:methylene chloride (80:20). For carrots and potatoes, two aliquots of the residue were applied to separate Florisil columns. Hexachlorobenzene (HCB) and chlorothalonil were eluted from one of the columns with hexane:methylene chloride (80:20) and methylene chloride:hexane:-acetonitrile (50:48.5:1.5), respectively. Pentachlorobenzonitrile (PCBN) was eluted from the second column with hexane:methylene chloride:acetonitrile (50:50:0.05). For celery, tomatoes, and cucumbers, two Florisil columns were also used, but chlorothalonil was eluted from one of the columns with methylene chloride:hexane:acetonitrile (50:48.5:1.5); from the second column, HCB was eluted with hexane:-methylene chloride (80:20) and PCBN with hexane:methylene chloride:acetonitrile (50:50:0.05 or 50:50:2.5).

To extract 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) and 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851), an additional aliquot of the acetone:sulfuric acid filtrate was treated with 2% paraffin oil in petroleum ether (potatoes, celery, and cucumbers) and diluted with water (carrots, potatoes, celery, tomatoes, and cucumbers). Acetone was removed from the filtrate by evaporation, 0.4 M sodium bicarbonate solution was added, the pH was adjusted to 4.5, then the solution was partitioned twice with petroleum ether; petroleum ether phases were discarded. The aqueous phase was adjusted to <pH 2, combined with sodium chloride (30%, w/v), and partitioned twice with diethyl ether. Ether extracts were combined and concentrated, then SDS-3701 was converted to its methyl ether derivative and SDS-46851 to its methyl ester derivative using concentrated hydrochloric acid:methanol (1:3) and diazomethane solution. The derivatized solution was concentrated, redissolved in methylene chloride, and applied to an alumina column. Methyl SDS-3701 was eluted with methylene chloride and methyl SDS-46851 was eluted with acetone:methylene chloride (50:50 or 70:30).

To isolate chlorothalonil, HCB, and PCBN from soybeans and wheat grain, samples were ground, then duplicate subsamples (50 g) were extracted with acetonitrile and filtered. An aliquot of the filtrate was diluted with water, combined with 10 N sulfuric acid, then partitioned twice with petroleum ether. Ether extracts were combined, concentrated, and cleaned up using Florisil column chromatography as described above for carrots. To isolate SDS-3701 and SDS-46851, additional subsamples were extracted with acetone:10 N sulfuric acid (95:5), partitioned, derivatized, and cleaned up using alumina column chromatography as described above for carrots.

Duplicate samples (1 lb) of whole cherries were extracted with acetone:10 N sulfuric acid (95:5) and filtered. An aliquot of the filtrate was treated with 2% paraffin oil in petroleum ether, then acetone was removed by evaporation. Sodium bicarbonate solution (0.4 M) was added, the pH was adjusted to 4.5, and the solution was partitioned twice with petroleum ether. To isolate chlorothalonil, HCB, and PCBN, petroleum ether extracts were combined, concentrated, and cleaned up using Florisil column chromatography as described above for celery. To isolate SDS-3701 and SDS-46851, the pH of the remaining aqueous phase was reduced to <2, sodium chloride was added, and the sample was partitioned twice with diethyl ether. Ether extracts were combined, concentrated, derivatized, and cleaned up using alumina column chromatography as described above.

All eluants were treated with 2% paraffin oil in petroleum ether, evaporated to dryness, redissolved in toluene, and analyzed using GC with electron-capture detection. The detection limits were 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. Recovery efficiencies from fortified plant samples ranged from approximately 60 to 130% of the applied for chlorothalonil, SDS-3701, and HCB; 50 to 140% for SDS-46851; and 65 to 140% for PCBN (Tables 1-A through 8-E).

DATA SUMMARY:

Chlorothalonil was variable, with no discernable pattern, in crops (carrot roots, potatoes, celery, soybeans, tomatoes, cucumbers, cherries, and wheat grain) which were harvested immediately after receiving four to sixteen spray applications, at 3- to 16-day intervals, of chlorothalonil (Bravo 720, 6.0 lb/gallon FlC) at 2.25-15 lb ai/A/application (3-20 pints formulation/A/application) and stored frozen for up to 1 year. Chlorothalonil ranged from 38.42 to 59.75 ppm in wheat grain, 5.94 to 36.31 ppm in soybeans, 5.11 to 22.63 ppm in cherries, 6.66 to 17.83 ppm in tomatoes, 3.21 to 13.92 ppm in celery, 0.79 to 4.79 ppm in potatoes, 0.47 to 3.11 ppm in cucumbers, and 0.75 to 2.70 ppm in carrot roots (Tables 9-A through 9-H). The degradates detected in the crops were

pentachlorobenzonitrile (PCBN),

4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701),

3-carboxy-2,5,6-trichlorobenzamide (SDS-46851), and

hexachlorobenzene (HCB).

PCBN was detected at 0.314-0.708 ppm in wheat grain, at 0.093-0.359 ppm in soybeans, at 0.077-0.287 ppm in cherries, at 0.072-0.208 ppm in tomatoes, at 0.068-0.135 ppm in carrot roots, at 0.034-0.135 ppm in celery, at 0.012-0.074 ppm in potatoes, and at up to 0.045 ppm in cucumbers. SDS-3701 was detected at 0.08-0.35 ppm in potatoes, at 0.09-0.23 ppm in wheat grain, at 0.04-0.16 ppm in carrot roots, at up to 0.16 ppm in celery, at up to 0.10 ppm in soybeans and tomatoes, at 0.01-0.07 ppm in cherries, and at ≤0.02 ppm in cucumbers. SDS-46851 was detected at 0.09-0.24 ppm in potatoes, at up to 0.14 ppm in celery, at ≤0.05 ppm in soybeans, at ≤0.04 ppm in carrot roots, at ≤0.03 ppm in cucumbers and cherries, and was not detected (<0.03 ppm) in tomatoes and wheat grain. HCB was detected at 0.011-0.021 ppm in wheat grain; at 0.004-0.013 ppm in soybeans; at up to 0.013 ppm in cherries; at ≤0.007 ppm in carrot roots, potatoes, celery, and tomatoes; and was not detected (<0.003 ppm) in cucumbers.

COMMENTS:

1. The experimental design used was not appropriate for determining the freezer storage stability of chlorothalonil and its degradates in the various plant matrices. Because the crops were field-treated, the initial quantity of chlorothalonil in each sample was variable, and degradation of chlorothalonil had already occurred prior to frozen storage. The appropriate method for determining the freezer storage stability of a test substance in a particular matrix involves spiking the matrix with a known amount of technical grade or purer test substance (chlorothalonil, SDS-3701, SDS-46851, HCB, or PCBN), then analyzing for the test substance and its degradates immediately posttreatment and after various lengths of time of frozen storage to determine if any degradation has occurred.

2. Detailed site characteristics (depth to the water table and slope of the field), field maintenance practices, and meteorological data (rainfall, irrigation, and air temperatures) were provided for each site in the original documents. The reviewer did not summarize the information since the study is unacceptable and because it would have required a considerable amount of time.

3. The initial 15 pages of MRID 41564821 were not available, but this did not preclude a review of the study. Pertinent information was obtained from Appendix II - Field Data.

Summary Table 1. Soil and site characterization plus field trial methodology.[a]

		%										
Location	Classification	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)	Plot size (sq feet)	Number of applications of Bravo 720	Rate (pint/A)	Dates of applications in 1988	Crop treated
Delavan, WI	"Muck sandy loam"	56	31	13	16	7.3	35.8	40 x 100	11	20	06/24-09/06	Carrots
Delavan, WI	Clay	20	31	49	5.5	7.4	27.6	40 x 100	15	15	06/15-09/26	Potatoes
Sturtevante, WI	"Muck loam"	44	36	20	13.9	5.5	39.3	20 x 100	16	3	06/15-10/03	Celery
Leonard, MO	Silty clay loam	18	50	32	1.6	6.3	19.9	100 x 100	8	20	07/21-10/24	Soybeans
New Holland, OH	Loam	36	39	25	2.7	6.2	14.3	30 x 50	8 1	3 9	06/08-08/09 08/09	Tomatoes
Columbus, OH	Loam	30	46	24	2.9	6.5	13	52.5 x 100	3 1	3 9	07/16-08/01 08/08	Cucumbers
Alton, NY	Sandy loam	72	20	8	2	6	6.7	60 x 84	10	4.125	05/09-07/18	Cherries
Leonard, MO	Clay loam	32	40	28	0.9	5.6	14.8	40 x 250	7	15	04/29/07/12	Wheat grain

[a] Information compiled by reviewer from field data provided in Appendix I (MRIDs 41564820-27).

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