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

DEC 5 1994

MEMORANDUM

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

SUBJECT: Chlorothalonil Reregistration: List A Case No. 0097: Chemical No. 081901: ISK-Biotech's Submission of Corn Field Trial and Processing Data: DP Barcodes D195757 & D195759: CBRS Nos. 12653 & 12651: MRID Nos. 429444-02 & -03.

FROM: William Smith, Chemist
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THROUGH: Edward Zager, Chief
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Attached is a review of chlorothalonil residue chemistry data submitted in response to the 9/6/91 Chlorothalonil DCI. This information was reviewed by Dynamac Corporation under supervision of CBRS, HED. The data assessment has undergone secondary review in the Branch and has been revised to reflect Branch policies.

The registrant has partially satisfied reregistration data requirements for chlorothalonil uses on field corn grown for seed and on sweet corn. The registrant must amend their end-use product labels containing uses for corn to remove the restriction on treatment of sweet corn grown for processing and to remove the feeding and grazing restrictions on corn forage, silage and fodder. Tolerances must be proposed on field corn grain, fodder and forage and on sweet corn forage and fodder. Additional field trial data must be submitted to support the tolerance proposals for field corn forage and sweet corn forage. Tolerances are not needed for corn processed commodities or for aspirated grain fractions.

Attachment: Registrant's Response to Residue Chemistry Data Requirements; D195759 & D195757; 1/7/94.

cc(with attachment): W. Smith (CBRS), Chlorothalonil Reg. Std. File, SF, RF, circulation, Dynamac.

7509C:CBRS:WOS:wos:CM#2:Rm805A:703-305-5353: 11/23/94

RDI: B. Cropp-Kohlligian 11/23/94, P. Deschamp 11/23/94, T. Edwards 11/23/94, S. Knizner 11/23/94, C. Olinger 11/23/94, M. Metzger 12/01/94, E.Zager 12/05/94.

DYNAMAC
CORPORATION
Environmental Services

Final Report

CHLOROTHALONIL
Shaughnessy No. 081901;
Case No. 0097
(CBRS Nos. 12651 & 12653;
DP Barcodes D195759 & D195757)

TASK 4
Registrant's Response to Residue Chemistry Data Requirements

January 7, 1994

Contract No. 68-D2-0053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA 22202

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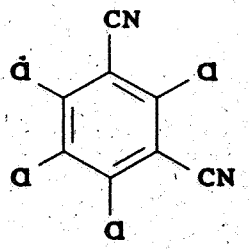
CHLOROTHALONIL



Shaughnessy No. 081901; Case 0097

(CBRS No. 12651; DP Barcode D195759)

(CBRS No. 12653; DP Barcode D195757)

Task 4

REGISTRANT'S RESPONSE TO RESIDUE CHEMISTRY DATA REQUIREMENTS

In response to a 9/6/91 Data Call-In Notice, ISK Biotech Corporation has submitted chlorothalonil residue data on field corn grain and fodder, corn grain processed commodities and aspirated grain fractions (1993; MRIDs 42944402 and 42944403). These submissions are reviewed in this report for their adequacy in fulfilling reregistration data requirements.

BACKGROUND

Chlorothalonil is registered for use on sweet corn and corn grown for seed to control foliage diseases such as Helminthosporium Leaf Blight and Rust. Label directions for corn prescribe applications of up to 1.5 lbs ai/A repeated at 4 to 7 day intervals or as required to maintain control. Applications are forbidden within 14 days of harvest as are applications to sweet corn to be processed. Labels also restrict grazing of livestock in treated fields or use of treated corn for silage or livestock forage. A tolerance of 1 ppm has been established for residues in or on sweet corn (K+CWHR) only.

The Agency has concluded (Residue Chemistry Chapter of Draft Chlorothalonil FRSTR, 1988) that the restriction on treatment of sweet corn grown for processing is not enforceable and that the restriction on grazing or feeding sweet corn forage is not practical since the utilization of sweet corn forage is under grower control only in FL. Therefore, in the Chlorothalonil DCI of 7/91 the Agency required that pertinent labels must be amended to remove the restriction on treatment of sweet corn grown for processing and to indicate that the feeding and grazing restrictions on sweet corn forage and fodder apply to FL only.

Additionally, a proposal of a tolerance for residues on sweet corn forage was required along with appropriate supporting field trial data.

In a DCI issued on 9/6/91 as an addendum to the 7/31/91 Chlorothalonil DCI, further data were required representing field trials and processing studies on field corn.

CONCLUSIONS AND RECOMMENDATIONS

1. The GC/ECD method used in the submitted corn studies is adequate for collecting data on residues of chlorothalonil, SDS-3701, and HCB in/on corn grain, corn fodder, and processed commodities of corn grain.

2. The storage stability of the analytical samples in the current submission are validated by 4-year storage stability data on wheat grain, peanuts, and soybeans (W. Smith; 8/5/94; CBRS No. 12403). No significant decline during storage of residues would be expected in the analytical samples in the present submission.

3. Chlorothalonil end-use product labels bearing use directions for corn must be amended. The restriction on treatment of sweet corn grown for processing and the feeding and grazing restrictions on corn forage, silage and fodder must be removed.

4. The registrant must propose tolerances for the combined residues of chlorothalonil and SDS-3701 in/on the following raw agricultural commodities:

   field corn grain
   field corn fodder
   field corn forage
   sweet corn forage
   sweet corn fodder

5. The submitted field trial data on corn grain and fodder (MRID 42944402) are adequate for purposes of proposing tolerances. However, additional field trial data are required depicting residues on field corn forage/silage and sweet corn forage/silage. The registrant should consult Follow-up Guidance for Number and Location of Domestic Crop Field Trials (found in Pesticide Reregistration Rejection Rate Analysis Residue Chemistry; EPA 738-K-94-001; June, 1994) before initiation of any new field trials.

6. The submitted corn grain processing study (MRID 42944403) is acceptable. No measurable residues of chlorothalonil, SDS-3701 or HCB were found in the grain or any processed fraction following the use of chlorothalonil according to label directions. A direct assessment of potential concentration of residues in milling products of corn could not be performed; however, CBRS concludes that the diversion of treated seed corn for food processing is not likely, given the premium

paid for seed corn compared with grain for processing. Furthermore, waste grain or screenings that could be used for livestock feed would not be acceptable for food processing. Therefore, no additional processing data or food/feed additive tolerances are required.

7. The aspirated grain fractions (grain dust) data submitted with the processing study (MRID 42944403) indicate that chlorothalonil and SDS-3701 residues can occur in grain dust at a potential combined level of 0.08 ppm. However, a tolerance for grain dust is not needed, as seed crop use is not expected to generate grain dust that would be diverted to livestock feed.

8. The appropriate level for tolerances for residues of chlorothalonil and SDS-3701 in meat and milk will be assessed on successful completion of ruminant feeding studies currently in progress. The present considerations on uses of chlorothalonil do not change our conclusion that tolerances are not needed for poultry and eggs.

DETAILED CONSIDERATIONS

Residue Analytical Methods

In conjunction with the current residue studies, ISK Biotech Corp. submitted concurrent method recovery data (1993; MRIDs 42944402 and 42944403) for chlorothalonil, SDS-3701, and HCB from corn grain, fodder, grits, meal, flour, starch, presscake, crude oil, refined oil, and aspirated grain fractions (grain dust). The GC/ECD methods employed for data collection in these studies are variations of Method I in PAM, Vol. II and a revised GC/ECD method, which has been validated by an independent laboratory. The method has been previously reviewed (W. Chin, 2/22/91) and includes provisions for the analysis of PCBN, HCB, and SDS-46851 as well as chlorothalonil and SDS-3701.

Residues in/on corn grain and fodder (MRID 42944402) are extracted with acidic acetone and the extract is partitioned with petroleum ether. Residues of HCB are extracted into the organic layer along with chlorothalonil and are separated by Florisil chromatography prior to GC/ECD analysis. Residues of SDS-3701 are methylated and then separated by alumina column chromatography prior to quantitation by GC/ECD.

Chlorothalonil/HCB and SDS-3701 are extracted separately from corn grain processed commodities (MRID 42944403). Chlorothalonil and HCB are extracted from grain, grits, meal, flour, presscake, and dust into acetonitrile and from starch into acidic acetone prior to partitioning into petroleum ether. Chlorothalonil and HCB are extracted from crude and refined oils into cyclohexane:methylene chloride (1:1, v:v) and cleaned up using gel permeation chromatography. Chlorothalonil and HCB are then separated by Florisil chromatography prior to GC/ECD analysis. SDS-3701 residues in non-oily matrices are

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extracted into acidic acetone and cleaned up by partitioning in petroleum ether prior to derivatization and GC analysis. For crude and refined oil samples, SDS-3701 is extracted into petroleum ether:0.4 M $NaHCO_3$ (1:1, v:v) and partitioned into the aqueous phase. SDS-3701 residues are then acidified, salinized, and partitioned into diethyl ether prior to methylation and GC analysis.

Concurrent method recoveries from the residue studies are presented in Table 1. The stated limits of detection were 0.01 ppm each for chlorothalonil and SDS-3701, and 0.00025 ppm for HCB.

These data indicate that the GC/ECD method is adequate for collecting data on residues of chlorothalonil, SDS-3701, and HCB in/on corn grain, corn fodder, and processed commodities of corn grain.

Table 1. Concurrent method recoveries of chlorothalonil, SDS 3701, and HCB from fortified control corn fodder, grain, and grain processed matrices.

Matrix	Compound	Fortification Range (ppm)	% Recovery	No. of Samples [a]
Corn fodder	chlorothalonil	0.03-50.0	86-123	13 (1)
	SDS-3701	0.03-1.0	70-100	11
	HCB	0.0005-0.05	78-138	9 (1)
Corn grain	chlorothalonil	0.03-1.0	81-107	12
	SDS-3701	0.03-1.0	87-95	12
	HCB	0.0005-0.05	80-124	14 (1)
Corn grain (processing)	chlorothalonil	0.03-1.0	90-105	6
	SDS-3701	0.03-0.5	83-96	6
	HCB	0.0005-0.01	89-126	6 (1)
Corn grits	chlorothalonil	0.03-1.0	95-103	6
	SDS-3701	0.03-0.5	82-107	6
	HCB	0.0005-0.01	86-99	6
Corn meal	chlorothalonil	0.03-1.0	88-100	6
	SDS-3701	0.03-0.5	87-103	6
	HCB	0.0005-0.01	88-108	6
Corn flour	chlorothalonil	0.03-1.0	95-110	6
	SDS-3701	0.03-0.5	93-126	6 (1)
	HCB	0.0005-0.01	97-108	6
Corn starch	chlorothalonil	0.03-1.0	92-103	6
	SDS-3701	0.03-0.5	87-98	6
	HCB	0.0005-0.01	100-110	6
Corn presscake	chlorothalonil	0.03-1.0	80-96	8
	SDS-3701	0.03-0.5	81-97	8
	HCB	0.0005-0.01	90-115	8
Corn oil (crude)	chlorothalonil	0.03-1.0	97-103	8
	SDS-3701	0.03-0.5	73-91	8
	HCB	0.0005-0.01	73-94	7
Corn oil (refined)	chlorothalonil	0.03-2.0	93-113	8
	SDS-3701	0.03-1.2	87-116	8
	HCB	0.0005-0.02	80-128	8 (2)
Corn grain dust	chlorothalonil	0.03-1.0	93-112	6
	SDS-3701	0.03-0.5	83-105	6
	HCB	0.0005-0.01	74-126	6 (1)

[a] Number of samples with recoveries outside the acceptable 70-120% range are indicated in parentheses.

Storage Stability Data

The samples of corn grain, corn fodder, and processed grain fractions in the submitted residue studies (MRIDs 429444-02 and -03) were stored frozen for up to 235 days between harvest and analysis. The data in the current submission are validated by 4-year storage stability data on wheat grain, peanuts, and soybeans (W. Smith; 8/5/94; CBRS No. 12403). No significant decline in any chlorothalonil residue was demonstrated over a 4-year period of frozen storage.

Magnitude of the Residue in Corn Grown Solely for Seed

ISK Biotech (1993; MRID 42944402) submitted data from six tests conducted in IL, IN, IA, MN, NE, and OH depicting residues of chlorothalonil, SDS-3701, and HCB in/on field corn fodder and grain harvested 45 days after the last of seven applications of the 6 lb/gal FlC or 82.5% DG formulation at 1.5 lb ai/A/application in ~20-30 gal/A, at 7-day intervals using ground equipment. The FlC formulation (Batch Number 029249) contained 53.6% chlorothalonil and 0.014% HCB. The DG formulation (Batch Number ASC-66518-0101-1207) contained 81.2% chlorothalonil and 0.029% HCB.

Duplicate grain and fodder samples were harvested from treated and control plots and were shipped frozen within 4 hours to Ricerca, Inc. for residue analysis. A grain sample from the IN test was also shipped frozen within 4 hours to Texas A&M University for a separate processing study.

Samples were analyzed 195-235 days after harvest using the GC/EC method described previously in this report. Concurrent method recoveries were 70-138% from fortified grain and fodder samples; details of the concurrent recovery data are available in Table 1 above. Limits of detection were 0.01 ppm for chlorothalonil and SDS-3701 and 0.00025 ppm for HCB. Apparent residues were non-detectable in all untreated forage and fodder samples, with the exception of a single control grain sample from IA that contained 0.0003 ppm of HCB.

Residues of chlorothalonil, SDS-3701, and HCB were each non-detectable in all treated grain samples, with the exception of one sample from IA yielding 0.03-0.04 ppm chlorothalonil in triplicate analyses. A duplicate composite sample from the same test bore nondetectable residues. Residue data for chlorothalonil, SDS-3701, and HCB in/on corn fodder are presented in Table 2. These data are consistent with chlorothalonil's mode of action as a contact fungicide. Residues were confined primarily to the fodder with mostly nondetectable residues on the grain. Combined residues of chlorothalonil and SDS-3701 on the fodder ranged from 2.6 ppm to 39.7 ppm with SDS-3701 comprising approximately 1% of the total residue. Residues of HCB were highly correlated with chlorothalonil residues, ranging from 0.0008 ppm to 0.011 ppm. The HCB/chlorothalonil ratio was the same in crop residues as it was in the formulations applied.

Table 2. Residues of chlorothalonil, SDS-3701, and HCB in/on corn fodder harvested 45 days following seven ground applications of chlorothalonil at 1.5 lb ai/A/application.

Formulation	Location	Residues (ppm)		
		Chlorothalonil	SDS-3701	HCB
6 lb/gal FlC	IL	4.82, 5.19	0.07, 0.08	0.0017, 0.0018
6 lb/gal FlC	IN	3.96, 4.85	0.03, 0.04	0.0021, 0.0024
6 lb/gal FlC	IA	14.3, 20.4	0.09, 0.09	0.0042, 0.0072
82.5% DG	MN	23.0, 23.3	0.17, 0.18	0.0077, 0.0093
6 lb/gal FlC	NE	2.56, 3.43	0.04, 0.05	0.00079, 0.00087
82.5% DG	OH	39.5, 22.5 34.2, 28.0	0.16, 0.11	0.011, 0.0064

The submitted corn grain and fodder residue data are adequate for purposes of proposing tolerance levels for corn grain and fodder. Current labels contain livestock feeding restrictions associated with uses on corn. It is now Agency policy (Table II [June 1994] of the Pesticide Assessment Guidelines, Subdivision O, Residue Chemistry) that livestock feeding restrictions on corn are undesirable and impractical. Therefore, the registrant must propose tolerances for the combined residues of chlorothalonil and SDS-3701 in/on corn grain, forage and fodder. These proposals must be supported by adequate field trial data. The data in the current submission, along with those submitted with Section 18 Exemption 91-IA-0003 (J. Abbotts; 8/27/91; D167032) indicate that a tolerance of 0.05 ppm would be appropriate for corn grain and a tolerance of 50 ppm would cover residues on fodder.

Magnitude of the Residue in Processed Commodities of Seed Corn

ISK Biotech (1993; MRID 42944403) submitted data from a processing study with corn grain. A grain sample was obtained from the test described above conducted in IN. Grain was harvested 45 days following seven applications of the 6 lb/gal FlC formulation at 1.5 lb ai/A. This rate is 1x the maximum registered rate for field corn grown for seed. Processing was conducted by the Engineering Biosciences Research Center of Texas A&M University. Following harvest, grain samples were stored for 112-132 days prior to processing into aspirated grain fractions (grain dust), grits, meal, flour, presscake, starch, crude oil, and refined oil. Processed fractions were stored for 39-164 days prior to analysis by Ricerca, Inc. using the GC/EC method described earlier in this report. Concurrent method recoveries ranged from 73-128%; details of recovery data and limits of detection are presented in the "Residue Analytical Methods" section above.

Two samples of each commodity were analyzed for chlorothalonil and HCB and two separate samples were analyzed for SDS-3701. Chlorothalonil, SDS-3701, and HCB were each nondetectable, <0.01, <0.01, and <0.00025 ppm, respectively, in/on four treated and four control samples of grain and each processed commodity. Two grain dust samples bore chlorothalonil residues of 0.05 and 0.07 ppm. A third grain dust sample contained SDS-3701 at 0.01 ppm.

This study is of limited usefulness in determining the potential for residue concentration in processed fractions from corn grain because the grain used contained no measurable residues. However, CBRS concludes that the diversion of treated seed corn for food processing is not likely, given the premium paid for seed corn compared with grain for processing. Furthermore, waste grain or screenings that could be used for livestock feed would not be acceptable for food processing. Therefore, no additional processing data or food/feed additive tolerances are required.

The submitted data indicate that chlorothalonil and SDS-3701 residues can occur in grain dust at a potential combined level of 0.08 ppm. However, a tolerance for grain dust is not needed, as seed crop use is not expected to generate grain dust that would be diverted to livestock feed (Aspirated Grain Fractions (Grain Dust): A Tolerance Perspective; E. Saito and E. Zager; 6/2/94).

Magnitude of the Residue in Sweet Corn

Data reviewed in the Residue Chemistry Chapter of the 1988 Draft Chlorothalonil FRSTR indicate that residues in or on sweet corn will not exceed the established 1 ppm tolerance when harvested 14 days following the last of multiple applications at the 1x rate. However, it was concluded that a label restriction on treatment of sweet corn grown for processing is not enforceable and that restrictions on grazing or feeding corn forage are not practical since sweet corn forage is under grower control only in FL. Therefore, in the Chlorothalonil DCI of 7/31/91, field trial data were required for the purposes of setting a tolerance on sweet corn forage. The DCI also required label amendments to remove the unenforceable restriction on treatment of sweet corn grown for processing and on feeding and grazing of sweet corn forage and fodder. The registrant has not responded to these data requirements.

The data requirements and label amendments specified in the 1991 DCI for sweet corn forage remain in effect with some revision. It is Agency policy that all livestock feeding and grazing restrictions on corn are undesirable and impractical. Therefore, all pertinent labels should be amended to remove all restrictions on feeding of sweet corn forage/silage and fodder. Also, sweet corn grain and fodder are now designated as raw agricultural commodities (Table II [June 1994] of the Pesticide Assessment Guidelines, Subdivision O, Residue Chemistry). The field corn grain tolerance, which must be proposed by the registrant will cover residues that would be expected to occur in sweet corn grain. Tolerances, which are supported by appropriate data, must be proposed for sweet corn forage and fodder to cover residues that might occur from registered uses on sweet corn.

Meat, Milk, Poultry and Eggs

At present there are no tolerances for chlorothalonil in animal commodities. Based on the data available, chlorothalonil residues are rapidly metabolized in animals and do not transfer to meat, milk, poultry and eggs (W.Smith; D199685; 10/14/94 and W.Smith; D196755; 11/2/94). On the other hand SDS-3701 is not significantly metabolized and represents the portion of the terminal residue that might transfer to animal commodities. According to the data in the present submission, SDS-3701 comprises about 1% of the total residue on corn commodities.

The registrant is currently conducting ruminant feeding studies (see D. McNeilly; D162243; 7/11/91 for review of protocol) in which separate groups of animals are being fed chlorothalonil (1.5 to 30 ppm) and SDS-3701 (0.1 to 2 ppm) for the purpose of establishing tolerances on meat and milk. The appropriate level for tolerances on meat and milk commodities will be determined on submission of an acceptable report on these feeding studies.

We have previously concluded, based on analysis of the TRR from poultry fed exaggerated levels of ^{14}C-chlorothalonil and ^{14}C-SDS-3701, that tolerances are not required for poultry commodities (W. Smith; D196755; 11/2/94). The potential level of chlorothalonil that may occur in poultry feeds from the established uses on corn do not change this assessment. The only change in poultry feed considerations is as a result of our conclusion that a tolerance of 0.05 ppm is necessary on grain. We consider it unlikely that significant quantities of seed corn will be diverted to poultry feed.

MASTER RECORD IDENTIFICATION NUMBERS

The citations for the MRID documents used in this review are presented below.

42944402 Dvorak, R.; Kenyon, R. (1993) Magnitude of Residues of SDS-3701 and HCB on Field Corn--1992: Lab Project Number: 5527-93-0068-CR-001: SDS-2787: 5527-93-0068. Unpublished study prepared by Dept of Environmental and Metabolic Fate, Ricerca, Inc. 809 p.

42944403 Fitzgerald, T. (1993) Magnitude of Residues of Tetrachloroisophthalonitrile (Chlorothalonil, SDS-2787), SDS-3701 and HCB on Processed Corn Fractions--1992: Lab Project Number: 5528-93-0090-CR-001: SDS-2787: 5528-93-0090. Unpublished study prepared by Dept. of Residue Analysis, Ricerca, Inc. 356 p.