EEB BRANCH REVIEW

4/28/76

DATE: IN _____ OUT _____ IN 3/24/76 OUT 4/28/76 IN _____ OUT _____

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. 201-EUP-50

PETITION OR EXP. PERMIT NO. 6E 1755

DATE DIV. RECEIVED _____

DATE OF SUBMISSION 3/8/76

DATE SUBMISSION ACCEPTED _____

TYPE PRODUCT(S): I, D, H, F, N, R, S

PRODUCT MGR. NO. L. Ziek

PRODUCT NAME(S) "SD-43775 Emulsible Concentrate Insecticide"

COMPANY NAME Shell Chemical Company

SUBMISSION PURPOSE "Insecticide for use on cotton"

CHEMICAL & FORMULATION Benzeneacetic Acid, 4-chloro-alpha-(1-methylethyl)-cyano(3-phenoxyphenyl)-methyl ester (SD43775)

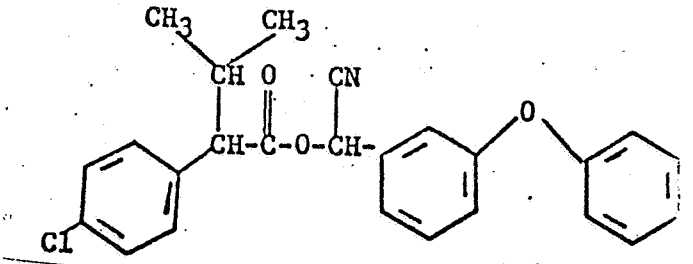
1.0 Introduction

1.1 This is the first EC-Review of the synthetic pyrethoid, SD-43775. The EUP proposes: testing sites (100) in 15 states; 4-thousand gallons of product containing 10-thousand pounds of ai. A total of 4,000-5,000 acres will be treated.

1.2 Emulsible Concentrate Insecticide, for Experimental Use Only; this is a 30% product containing 2.4 lbs ai/gallon.

1.3 Physical and chemical properties (Section A). Section D, Tab 14 (pg 3), Notes the ai is mixture of two isomers.

Structure:



Empirical Formula: $C_2H_{22}ClNO_3$

Molecular Weight: 419.9

State at 23°C: Yellow oil

Odor: Mild, chemical

Viscosity:

Centipoises	t°C
39300	23
4320	39
400	59

Density: 1.17 g/ml at 23°C.

Solubility: in water <20 ul at 20°C

2.0 Directions for Use on Cotton.

For ground or air application, mix the recommended amount with sufficient water to provide uniform coverage - the rates vary from 2.7 to 10.7 fluid ounces of product (0.05 to 0.20 lb ai) per acre, depending on the pest. (Maximum number of applications 10-12; Sect G. Page 2)

Restrictions:

Repeat as necessary to maintain control. Do not apply within 21 days of harvest. Do not graze livestock on treated fields or feed treated trash.

1.0 Introduction

1.1 This is the first EC-Review of the synthetic pyrethoid, SD-43775 The EUP proposes: testing sites (100) in 15 states; 4-thousand gallons of product containing 10-thousand pounds of ai. A total of 4,000-5,000 acres will be treated.

1.2 Emulsible Concentrate Insecticide, for Experimental Use Only; this is a 30% product containing 2.4 lbs ai/gallon.

1.3 Physical and chemical properties (Section A). Section D, Tab 14 (pg 3), Notes the ai is mixture of two isomers.

Structure:

Empirical Formula: $C_{22}H_{22}ClNO_3$

Molecular Weight: 419.9

State at 23°C: Yellow oil

Odor: Mild, chemical

Viscosity:	Centipoises	t°C
	39300	23
	4320	39
	400	59

Density: 1.17 g/ml at 23°C.

Solubility: in water <20 ul at 20°C

2.0 Directions for Use on Cotton.

For ground or air application, mix the recommended amount with sufficient water to provide uniform coverage - the rates vary from 2.7 to 10.7 fluid ounces of product (0.05 to 0.20 lb ai) per acre, depending on the pest. (Maximum number of applications 10-12; Sect G. Page 2)

Restrictions:

Repeat as necessary to maintain control. Do not apply within 21 days of harvest. Do not graze livestock on treated fields or feed treated trash.

STORAGE AND DISPOSAL

Store in a secure, dry and temperature area. Avoid contact with water, feed or food. Do not use or store around the home. Destroy used containers per local and federal regulations.

Any unused SD 43775 will be taken back by Shell Chemical Company at the end of the season (Section G, Page II)

3.0 Discussion of Data

Note: The labelled studies were done with "^{14}C" in the chlorophenyl ring of the ai (Sect C, tab 25).

3.1 Analytical Methodology (Volume 5, section D(1), tabs 11, 12, 13, 14).

GLC-procedures (4) are described in detail.

Tab	Column	detection	Ring	Recovery	Sample *
11	OV-101	EC	0.2-0.02 (ppm)	85%	Cotton seed
12	OV-101	flame	0.5	90%	Cotton seed
13	OV-101	flame	0.5-20	-------	soil

* Cotton samples were extracted with hexane and acetonitrile, or acetonitrile directly; the soils, with acetone - hexane (1.1). Clean up; an activated Florisil column is recommended.

Tab 14 presents data showing common pesticides (9) do not interfere.

Conclusion

These GLC procedures should be adequate to determine SD-43775 residues in the following EC-studies.

3.2 Degradation of ^{14}C-(chlorophenyl)-SD 43775 during exposure to soil under Aerobic, Anaerobic, and Steril conditions [Sect. C, tab 3D; Vol II-B (Vol 3 of 6)].

Haniford sandyloam soil samples (150 gm) were moisten, spiked (2.5 ppm) with "^{14}C-SD 43775", and stored under greenhouse conditions for 30-days. The controls were steam sterilized.

Aerobic samples received two hal-hour aeration per week. The Anaerobic series was started after 30-days with samples from the aerobic study; the converted sample were stored under nitrogen for an additional 60 days. Acetone extracts of the samples were subject to TLC and radio assay (LSC).

Summary

TLC WORK: initially 99% of the extractable activity was SD 43775, after 90 day only 90% was SD 43775; a 10% of decline. The degradates (2 or 3) were noted to be more polar than the parent.

Parent Soil Residues (ppm) Based on "^{14}C" (from Table 1)

Days	Aerobic (Avg.)	Anaerobic (Avg.)	Sterile (Avg.)
0	2.51	-a)	-a)
15	2.44	-	-
30	2.38	-b)	2.54
60	2.24	2.40	2.50
90	2.07	2.06	2.32[c)]

A) All samples were prepared identically at the same time. Hence, data listed is "Aerobic" columns are 0 time controls for all treatments.

B) Samples were kept for 30 days after treatment under aerobic conditions before anaerobic conditions were established. Zero time same as "Aerobic" at 30 days.

C) Samples contaminated with microorganisms.

Conclusions

(a) Aerobic and anaerobic degradation rates on Handford sand loam are similar.

(b) The degradation products are not adequately identified.

(c) Soil microorganisms appear to participate in the degradation of SD 43775 in this study.

3.3 Dissipation of SD 43775 in Soil at Wenatchee Washington [Sect. D, Tab 8 Vol I (5 of 6)]

The ai was applied at two different rates (0.5 or 2.5 lbs per acre) as a mix with paraquat (0.25 lb per acre). The applications were to field plots (20' X 20'): Wenatchee, Washington (sand 65%, silt 25%, clay 10%). Shell is GLC- procedure MM-R-425-1 was used to determine ai-residues (see 3.1).

SD-43775 Residues*

Day	Control	0.5 lb a/acre	2.5 lb a/acre
0	<0.01 ppm	0.25 ppm	2.5 ppm
7	--------	0.17	1.5
20	<0.01	0.13	1.2
90	-------	0.08	0.2

* 3-inch cores: parent residues

Conclusion:

(1) The ai-halflife (parent) in these field-soils approximates 30 days, degradation products are not identified.

(2) the depth taken was only 3 inches, Paraquat was also applied and test was not made in a cotton growing area (Sect 3.3.1)

3.3.1 Dissipation of SD-43775 in Soil at Monroe Louisiana [Sect D, Tab 9, Vol I (5 of 6).

The ai was applied at two different rates (0.5 and 2.5 lbs/acre) only one application was made. Application was to a silt loam soil at Monroe, La.; the plots were 50-feet by 8-rows wide. Shell's GLC procedure MMS-R-425-1 was used to determine parent soil-residues (see 3.1).

SD 43775 Residues*

Day	Control	0.5 lb a/acre	2.5 lb a/acre
1	0.01 ppm	0.32 ppm	1.5 ppm
8	---------	0.14	0.95
19	---------	0.4	0.86

* 3-inch cores; parent residue

Conclusion

The parent-halflife varies from 12-days (0.5 lbs) to 24-days (2.5 lb); the study is acceptable.

3.4 Photochemical Degradation of SD 43775 on Silica Gel, Glass, Soil, and in Water [Section C Tab 26; Vol II-B; (3 of 6)].

1) Irradiation of thin-layers on silica

TLC-plates were prepared and spotted with "^{14}C-SD 43775". The testing included sensitizers (4), the usual darkness controls and dieldrin as a positive control. The plates received continuous inside exposure (1760 ft lamberts); or outside sun (5400 ft lamberts), 8-hour each day. After irradiation the plates were chromatographed and separated fractions were radioassayed. Excerpts from the data are summarized.

Summary (figure in %)

TLC Zones	Inside (Table 1) Dark 7 da	Dark 28 da	Sensitized (*) 7 da	Sensitized (*) 28 da	Unsensitized 7 da	Unsensitized 28 da	Outside (Table 6) Unsensitized 7 da	Unsensitized 28 da
Origion	6.0	19.8	17.7(3)	23.9(2)	17.3	30.3	16.5	27.6
Fractions (No)	0.3(3)	0.3(3)	5.1(3)	15.1(4)	2.6(3)	6.3(3)	13.3(3)	19.4(5)
ai	86.7	73.9	73.1	31.5	75.0	48.9	57.8	25.4
Less polar (No)	0.3	0.4	2.1	6.5	1.0	2.1	3.9(2)	2.7(3)
Recovery (Avg)**	93.3	94.5	97.8	77.0	95.5	87.7	91.6	75.0

* Benzophenone figures from table 3; the pattern of increased degradation is similar to that of the other (3) sensitizers.

** Average of duplicates

Conclusion

(a) The darkness control figures indicate instability of the ai on silica - the half life extrapolates to ~~CA~~ CA 41 days

(b) Correcting for degradation by the controls, the photo-half life under vitalight (intensity 1/3 of sunlight) was ~~CA~~ CA 1,300 hrs; in sunlight ~~CA~~ CA 210 hrs.

(c) Photoproducts are not adequately identified.

2) Irradiation of thin-layers on soil

TLC-plates were coated with Handford sandy loam, spotted with "^{14}C-SD 43775", and then exposed to sunlight for 28-days. The resulting degradation was similar, but proceed at a slower rate, to that observed on silica.

Summary of Data (Table 17)

TLC Zones	Dark Control 7 days	Dark Control 28 days	Irradiation 7 days	Irradiation 28 days
Origion	4.0%	8.2%	8.2%	16.2%
Fractions (No)	3.3 (3)	10.4(4)	3.8(4)	3.8 (?)
ai	81.7(2)	70.1	61.2	48.2
Less polar (No)	0.4(2)	0.4(2)	20.2(2)	2.3 (?)
Recovery	81.5	lost	81.3	77.8

Conclusion

(a) The photoproducts are not adequately identified.

(b) The ai-halflife was about 63 days (extrapolation) or 500 hrs.,

3) Photodegradation on Glass.

Films of "^{14}C-SD 43775" were prepared in petri dishes by evaporation from acetone solution. The dishes were covered with saran and irradiated; outdoor exposures were for 8-hr each day.

Summary of Sunlight Testing (excerpts from tables 13,14)

TLC Zones	Darkness Control 1-day	Darkness Control 4-day	Irradiated Sample 1-day	Irradiated Sample 4-day
Origion	0.4%	0.4%	4.1%	19.9%
Fractions (No)	1.9(4)	1.9(4)	4.5(3)	17.9(4)
ai	94.8	96.4	84.1(2)	41.1
Less polar	0.7(2)	0.8(2)	0.9(2)	1.9
Recovery	97.6	99.4	93.7	81.5

Conclusions

(a) The photo-half life of the ai was ~~CA~~ ca 30 hours.

(b) The photoproducts are not adequately identified.

4) Photodegradation in Acetone solution (2%) and in Water (as a suspension)

A suspension of "^{14}C-SD 43775" (1-ppm) was prepared with xylene (CA 0.5%) and emulsifiers (CA 0.3%). Degradation in acetone soln was initially rapid (CA 8X the suspension rate), but declined. Rates were approximately the same in both solutions at the end of the testing period. Samples were analyzed by TLC, after ethyl acetate extraction.

Summary of Sunlight Exposures in Water (excerpts from Tables 19, 20)

TLC Zones	Darkness Control			Irradiated Samples		
	1-day	18-day	28-day	1-day	18-day	28-day
Origion	0.1%	0.2%	0.8%	0.7%	6.6%	8.6%
Fractions (No)	4.3(5)	1.5(5)	2.6(5)	3.9(5)	18.9(5)	21.5(5)
ai	85.3	75.0	77.2	79.2	49.9	47.9
Less polar (No)	0.2	0.4	0.5	0.9	4.4	3.4
Extd. recovery	89.6	77.2	81.2	84.6	79.5	81.5
Water; Aft. Ext.	2.6	11.1	0.4	6.3	2.4	2.0

Conclusion

(a) Photo-half life in water, extrapolating and correcting for degradations by the control, was about 500 hours

(b) Photoproducts are not adequately identified.

3.5 Residue Data for SD 43775 in Rotational Crops (alfalfa, potatoes, wheat, soybean) from A Simulated Rotational Study (Calif.). [Section D, Tab 10; Vol I (5 of 6)]

SD-43775 was applied at either 0.1 or 0.5 lbs per acre, with Dacthal (6 lbs/A), to a sandy loam (OM 1%). The application was on 5/5/75; crops were planted 6/5/75; sampling was on 9/12 (126 days), except for alfalfa, 7/29 (82 days). The samples were stored frozen from collection date until analysis (1/76). SD-43775 was determined by a modification of shell's procedure for SD-43775 in cotton (Tab 12).

Summary and conclusion: SD-43775 Residue were less than 0.01 ppm; Recoveries Ranged 70-90%, at 0.02-0.1ppm

This is not adequate rotational crop study. It was a cold study. Only one application of SD 43775 was made about 1 month before planting. Multiple applications (10-12). Analytical method is for parent compound only.

3.5 Investigation on the Transport of 14C-(chlorophenyl)-SD 43775 from Treated to Untreated Leaves on Cotton Plants [Sect. C, tab 28, Vol II-2 (3 of 6)]

Single leafs (10) of greenhouse cotton plants (10) were treated with "14C-ai" (49 mmgm's) in aqueous aceton solution. One application was made to either upper or lower leaves of the plants. After 15 days, leaves below and above those treated showed no significant activity; the 14C-combustion procedure had a sensitivity of 0.002 mmgm's per leaf. Assays of the treated leaves are not reported. However, similar studies (see 3.6) indicate the "14C-Residues-half life" in the leaf is about 35 days. The studies together (3.5; 3.6) indicate SD 43775 (parent) will not translocate when applied to the fuliage of cotton.

3.6 Disappearance of "14C" from Cotton Leaves Treated with 14C-(chlorophenyl)-SD 43775[Sect C, tab 27; Vol II-2 (3 of 6)]

Leaves of acala cotton plants, grown in an outside enclosure, were treated with 240 mmgm's of the "14C-ai" by either a single or double application. The 2nd application of 120 mmgm's was made after 3-weeks. The treated leaves were analyzed periodically. Acetone extracts of the leaves were assayed (LSC); unextracted "14C" was determined by combustion. The following data, from Table 1 is similar to that obtained in the double treatment.

Summary of Single treatment Data (from Table 1)

Day	14C-Extracted	14C-Unext.	total
0	184 mmgm	36 mmgm	220 mmgm*
23	136	29	165
49	71	22	93
101	31	28	59

* Recovery 91.7%

Conclusion:

The residue-half life of "14C-SD 43775" in cotton foliage is shown to be about 35 days - degradation products were not identified.

3.7 Residues of "14C" in Milk and Tissues from Cows Fed "SD 43775-14C" [Sect C, Tab 31; Vol II-13 (3 of 6)]

Lactating Guernsey were dosed daily with "14C-(chlorophenyl)-SD 43775" for 21 days; dosing was equivalent to rations with "ai" at 0.11 ppm. Most of the activity was eliminated in feces (36%) and urine (28%). Residues in brain, muscle, fat, and organ tissues was less than 0.02 ppm. About 1% of the activity was present in milk and work was done with butterfat to characterize the metabolites. That is; 14-day and 21-day composite samples were cleaned-up with hexame and acetonitrile; the acetonitrile extract (90% recovery) was subject to TLC; Activity in the separated fractions was determined - characterization of metabolites is not adequate.

Conclusion

(a) About 30% of the dose was not recovered.

(b) Metabolites were not characterized.

3.8 Residues of "14C" in Eggs and Tissues from laying Hens Fed "SD 43775-14C" [Sect C, Tab 32, Vol II-B (3 of 6)]

White leghorn hens were Fed "14Cai-Rations" (0.03 ppm) for 32-days. The resulting residues (14C) in blood, fat, meat, organs, etc., were at the detection level (0.004 ppm). Metabolites were not characterized.

3.9 Residues of "14C" and "SD 43775-14C" in Fish Exposed to "SD 43775-14C" [Sect C, Tab 33; Vol II-B (3 of 6)]

Rainbow trout (10-16) weighing between 20 to 30 grams, normally maintained, were exposed to "14C-ai" (0.20-0.27 ppB) for periods of 35-days or less; tanks, 3-liter; pH 7.9-8.5; 11-13°C. The water was aerated and the fish ere transferred to freshly treated water at intervals of 3 to 4 days. Testing was followed by a withdrawal period of 33 days. A single analysis of 'Group II' fish at 35 days showed Residue of 0.087 ppm equivalent a.i.

Summary of Edible Residue Data (from Table 3)

Days	^{14}C Residues[a] ppm Equivalents	SD 43775 Residues[b] ppm
Exposure Interval:		
5	0.017 ± 0.0004	0.017
10	0.022 ± 0.003	0.019
20	0.050 ± 0.002	0.041
35	0.055 ± 0.007[c]	0.050
Clearing Period:		
19	0.038 ± 0.006[c]	0.031
33	0.030 ± 0.002[c]	0.029

11

a) Mean ± Probable Error of Mean.
b) Determined by GLC equipped with electron capture detector.
c) Each fish analyzed separately prior to being composited for GLC analysis.

Conclusion

(a) The "14C" and GLC-Residue Figures agree.

(b) Withdrawal-halflife approximates 35 days.

(c) The study is not satisfactory - A longer study is needed, since the Residues did not plateau. The accumulation factor exceeds 300.

(d) No analysis of residues in VISCERAL tissue.

4.0 Summary

4.1 [A] We have received a study (see 3.5) which does not provide sufficient data to assess hazard to rotational crops. Further, the possibility of such residues is not clear from the soil persistence data (4.4.1) Aged leaching data has not been submitted.

4.2 [B] Mobility data: none

4.3 [C] Accumulation in the food chain: the data is not adequate (See 4.4.6) to assess the probability of accumulation.

4.4 Brief summary of data.

4.4.1 Soil persistence: the field study (3.3) indicates the parent-halflife CA 1-month; however the aerobic study (3.2) indicates the parent-declines 17% in 90-days.

4.4.2 Hydrolsis data: none

4.4.3 Photostability

(a) The parent-halflife, as a thin layer in sunlight, varied with the surface: on glass, 30-hours; on silica, 80-hours; on soil, 500-hours.

(b) In solution, as a water suspension, parent-halflife was CA 500-hours.

(c) The photo-products are not acceptably identified in any of these studies.

4.4.4 Studies to show the effect of the ai on the activities of soil organisms is needed.

4.4.5 Rotational - crop data is needed.

4.4.6 Accumulation in fish: The study submitted (3.9) did not clearly plateau; a longer study is needed; the carcass in this work refers to edible tissue carcass (eviscerated fish minus heads and tails) accumulation factors exceeds 300. Further, on withdrawal the residues decline slowly, the withdrawal - half life exceeds 30 days.

Recommendations

5.1 We can go along with the permit providing a 12-month rotational - crop restriction is added to the label. So as "do not rotate treated area within 1 year of last application except with cotton".

5.2 The studies submitted with the permit had deficiencies which must be supported with the following data prior to registration.

(a) The major and minor degradation products, by chemical name and structure, are needed for each study. Material balance data should accompany radiolabelled studies.

(b) The rotational and/or subsequent crop residue study was not adequate. A study conducted with the following protocol and radiolabelled SD-43775 would provide the needed data.

1. For crops rotated immediately after harvest of a crop in the treated area, the pesticide is to be aged in a sandy loam soil under aerobic conditions for about 120 days, then the soil planted to a root crop, small grain, and a vegetable. The root crop is required; however, crops in two other crop groupings may be substituted for the small grain and vegetable.

2. For crops rotated the following year after treatment, the pesticide is to be aged in the soil for one year prior to planting. Crops should be as above.

3. If significant residues are found, then actual field studies using non-labeled pesticide will be required. Such data must be obtained under actual agricultural practice.

4. If residues are found in rotational and/or subsequent crops in the field, then a labeling restriction will be needed. This restriction will take the form of a time interval from application to planting of rotational crops such that illegal residues will not occur in the rotational crop. A restriction longer than 18 months is not acceptable.

5. Cover crops can be rotated if label restrictions are such that the cover crop is plowed under and not grazed.

6. If the agricultural practice is such that a treated crop area is rotated with another crop that will result in another treatment of the pesticide to the same area, residue data will be required on the second crop. The rotational crop is to be grown under actual use conditions.

(c) Submit additional data to show a plateau occured in the group II fish residue study (Section C, Tab 33): or provide a longer study. The following protocol will provide the needed data.

A fish accumulation study is needed on catfish.

A. A sandy loam is to be treated in a way that catfish would be exposed to 0.01 ppm and 1.0 ppm. The labeled pesticide is to be aged in soil under aerobic conditions for 30 days prior to fish exposure. If a rice use is anticipated then the labeled pesticide should be aged in the soil under water for 30 days prior to fish exposure.

B. Catfish are to be exposed to treated soil for 30 days. If a plateau level has not been reached then exposure should be extended for an additional 30 days.

C. The rate of residue dissipation is to be determined by placing the catfish in a pesticide free environment at the end of exposure time.

D. Residue determination of edible tissue are needed throughout the study. When a plateau level is reached or at an interval of high residues in the edible tissue, determination for poplar and nonpoplar extractable residues are needed along with determination of unextractable residues. Determination for residues in viscera should be made at several intervals to correspond with other sampling intervals. Identity of residues present in fish should be made at plateau, highest accumulation level and at 2 weeks during withdrawal. This also applies to soil and water taken with fish samples.

E. Accumulation factors should be recorded.

F. Determination for amounts of residues present in water and in soil should be made and sampled along with catfish samples.

G. In some cases identification of residues in fish tissue will be needed.

NOTE: All radiolabeled studies should be supported with the following information:

a. Sample calculations;

b. Counting efficiency;

c. Counting time;

d. Background levels;

e. Probable error with scintillation techniques.

5.3 All other environmental chemistry data required by Section 3 of the Regulations must be either submitted or referenced prior to Registration.

Ronald E Ney, Jr 5/7/76

Ronald E. Ney, Jr. 4/28/76

E B Britten

E. B. Britten 4/27/76
Environmental Chemistry Section
EEE Branch

5.4 Soil degradation and dissipation studies should continue until a 90% loss of parent is reached, and until patterns of degradation, build-up and decline, are established. The amount of bound residues are to be determined.

~~(d) Soil degradation and dissipation studies should continue to 2 times of 90% loss of parent and until patterns~~

~~the pattern of buildup and decline of the degradation products.~~

(d) Soil degradation and dissipation studies should continue until a 90% 10% of parent is reached and until patterns of degradation, buildup and decline, are established. The amount of bound residues are to be determine.

5.3 All other environmental chemistry data required by section 3 of the regulations must be either submitted or referenced prior to registration.

Ronald E Ney, Jr 4/28/76

E.R. Butler 4/27/76
Environmental Chemistry Section
EEE Branch