

109301

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Review Section No. 1
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Attached please find the environmental fate review of:

Reg./File No.: 201-URI

Chemical: Pydrin

Type Product: Insecticide

Product Name: SS-Pydrin® Insecticide

Company Name: Shell Chemical Co.

Submission Purpose: Review data for New Technical ingredient
and formulation

ZBB Code: Other

ACTION CODE: 165

Date in: 7/26/84

EFB # 4476

Date Completed: 9/11/84

TAIS (level II) Days

63

3

Deferrals To:

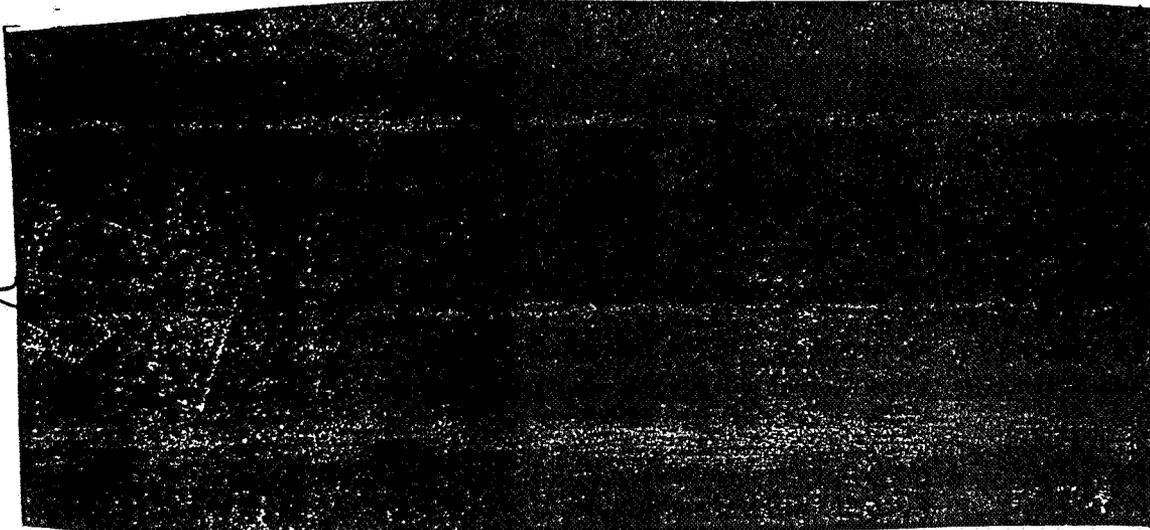
Ecological Effects Branch

Residue Chemistry Branch

Toxicology Branch

1.0 INTRODUCTION

Shell Chemical Co. has submitted applications for registration of technical SS PYDRIN® (MO 70616) and of SS PYDRIN® Insecticide 1.9 Emulsible Concentrate, both having fenvalerate as the active ingredient.

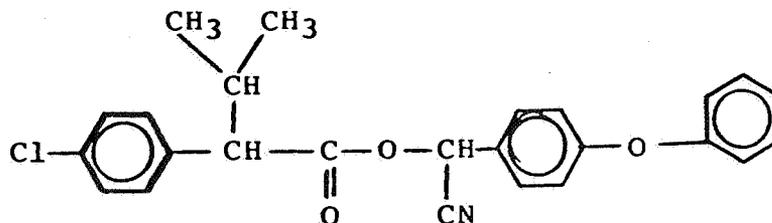


1.1 Chemical

Common name: Fenvalerate

Chemical name: Cyano-(3-phenoxyphenyl) methyl 4-chloro-alpha-(1-methylethyl)benzene acetate

Chemical structure:



2.0 DIRECTIONS FOR USE

The proposed use directions are appended to this review. Basically, the use rates for the currently registered PYDRIN® 2.4 EC formulation are reduced by one-fourth in the proposed PYDRIN® 1.9 EC formulation. The proposed rates range from 0.034 to 0.45 lb. a. i per acre per season.

3.0 DISCUSSION

3.1 Data previously reviewed indicated that (racemic) fenvalerate degrades by photolysis, in aerobic and anaerobic soil under laboratory conditions, and in soil under field conditions. It is stable to hydrolysis.

3.2 Considering the fact that the application results in a reduced amount of fenvalerate applied (albeit primarily the SS-isomer rather than the racemic mixture), EAB does not consider additional environmental fate data are necessary to support the proposed change.

However, data included in the current submission were assigned EPA Acession No. 254113 and are briefly described here. These studies (except 3.3.6, below) have not been reviewed as per the Standard Format For Data Evaluation.

3.2.1 Degradation of Pyrethroid Insecticides in the Field., J. Miyamoto and N. Mikami (Sumitomo Chemical Co.), Proceeding of the 5th International Congress of Pesticide Science 5, 225, 1980. Tab 1.

This article is not reviewed here. It is a survey review of the class of pyrethroids including permethrin, cypermethrin, deltamethrin, fenvalerate and fenprothrin. As such, it does not contain sufficient experimental detail for review. Three fenvalerate studies were referenced, two of which are included elsewhere in the submission. The third reference is to another survey review article.

3.2.2 Photodegradation of Fenvalerate (Sumicidin®) in Water and on Soil Surface. Mikami, N., N. Takahashi, K. Hayashi, and J. Miyamoto (Sumitomo Chemical Co.), J. Pesticide Sci. 5, 225-236 (1980). Tab 2.

Procedure

Solution: Filter sterilized distilled water, 2% aqueous acetone, river (pH 7.8) and sea water (pH 8.0) were fortified to 0.05 ppm with suspensions of ^{14}C -CO-(2RS, 1RS)-fenvalerate labeled in the CO group and ^{14}C -CH-(2S, 1RS)- and ^{14}C -CN-(2S, 1RS)-fenvalerate labeled in the CH of the benzyl group and CN, respectively. Tween 85 was used as emulsifier.

Soil: Soil TLC plates of sieved (to 2mm) soils, Kodiara light clay, Kantano sandy loam and Azuchi sandy clay loam were spotted with $^{14}\text{C}_\alpha$ - or ^{14}CN -fenvalerate at a concentration of 0.55-0.59 $\mu\text{g}/\text{cm}^2$. The TLC plates were exposed to natural sunlight during September, 1978. As control, soil TLC plates were held in darkness.

Conclusions

The data show that ^{14}C -(SS)-fenvalerate (in a 50% mixture with the ^{14}C -(SR)-fenvalerate) photodegrades with cleavage of the ester bond as the major route of degradation. Phenoxybenzoic acid and 2-(4-chlorophenyl)isovaleric acid were the major intermediate photodegradation products in aqueous solution. $^{14}\text{CO}_2$ was the final degradation product. CONH_2 -fenvalerate (SD 47114) was the major soil photodegradation product.

(Note: The authors reference a study wherein decarboxy-fenvalerate was the major photodegradation product when fenvalerate was irradiated with UV light (>290 nm) in an aqueous acetonitrile solution.)

3.2.3 Metabolic Fate of Fenvalerate (Sumicidin®) in Soil and by Soil Microorganisms. H. Ohkawa, K. Nambu, H. Inui and J. Miamoto. Sumitomo Co. report. J. Pesticide Sci., 3, 129-141 (1978). Tab 3.

This study was reviewed by EAB 5/11/78 and found deficient in satisfying the requirement for soil metabolism study. However, subsequent studies were submitted and favorably reviewed.

3.2.4 Metabolic Fate of Fenvalerate (Sumicidin®) in Bean Plants. H. Ohkawa, K. Nambu, and J. Miyamoto (Sumitomo Chemical Co.). J. Pesticide Sci., 5, 215-223 (1980). Tab 4.

This study reports on the metabolism of isomers of fenvalerate in bean plants when applied to leaf surfaces. Plants were maintained under laboratory conditions. This study is not relevant to environmental fate review and is not reviewed here.

* All Tables and Figures in this review are taken from the registrant's current or previous submissions.

3.2.5 Bioaccumulation and Biodegradation of the (S)-Acid Isomer of Fenvaleratē (Sumicidin®) in an Aquatic Model Ecosystem. H. Ohkawa, R. Kikuchi and J. Miyamoto. (Sumitomo Chemical Co.), J. Pesticide Sci. 5, 11-22 (1980)

A portion of this report deals with exposure of carp (Cyprinus carpio LINNES) to ^{14}C -(S)-fenvalerate for up to 7 days. Those fish exposed for 7 days were then transferred to clean water changed daily. Water samples were taken during the exposure period. Residues in water and whole fish were extracted with methanol and then analyzed by TLC. Duplicate fish tanks were held in a greenhouse and maintained at $24 \pm 2^\circ$.

Note: Data on a model ecosystem containing fish, snails, daphids and algae were also presented.

Conclusions

While this study is not acceptable as a fish accumulation study for satisfying the environmental data requirement, EAB notes the results of this part of the study. The maximum EAB calculated bioaccumulation factor was 1844X. Approximately 87% of the accumulated residues were eliminated during the clearing period, with a clearing half-life of about 5 days.

3.2.6 Photodegradation of SD 43775 on Soil Thin Layers. A. Ehmann and J. M. Ingamells. April 14, 1981. Shell Report No. RIR-22-002-81. Tab 6.

Soil thin layer plates were prepared with Hanford sandy loam soil (81.6% sand, 11.2% silt, 7.2% clay, 1.06% organic matter, pH = 7.3, CEC = 7.5 meq/100 gm, 1.37 g/cc bulk density). Soil was sieved through 0.0178 mm (80 mesh) wire screen. A slurry was made with water and applied to glass plates to a thickness of 1 to 1.5 mm. Plates were then air-dried. SD 43775 (racemic ^{14}C -fenvalerate) was applied to soil at a rate equivalent to about 0.3 lb. a. i./A.

Soil plates were exposed to either artificial or natural sunlight. Artificial light was with fluorescent tubes. Exposure was for 14 hours followed by 10 hours darkness. Temperature of the soil ranged from $39.5 \pm 1^\circ\text{C}$ (light) $29.0 \pm 2.0^\circ\text{C}$ (darkness). Spectral irradiance of the light source was measured with a spectroradiometer.

Exposure to natural sunlight was conducted by (1) with the TLC plate mounted onto a solar photoreactor which tracked the sun from sunrise to sunset ("tracking plate") or (2) the plate in a fixed position ("non-tracking plate")

Soil was exposed for 6, 12, 24, and 48 days. After exposure soil areas were scrapped from the plates and extracted with methylene chloride, acetone, acetone:water (4:1; v:v) and methanol:water (4:1; v:v). The extracts are identified as follows: The methylene chloride and acetone extracts were combined and redissolved in acetone (extract 1A); aqueous acetone extract was redissolved in acetone (extract 1B); the acetone insoluble material (extract 2); the methanol:water extract was redissolved in methanol (extract 3) and the methanol insoluble material was redissolved in methanol:water (extract 4).

Extracts 1A and 1B were cleaned up by TLC and ^{14}C areas identified by autoradiography (zones 1-5). The radioactive areas were then eluted from the silica gel with acetone:water (4:1, v:v).

Extracted ^{14}C in the various extracts was quantitated by LSC. Solvent extracts of 1A and 1B, alone and combined were further analyzed by GC and GC-MS. Some fractions were methylated by trimethylsilylation for additional GC/GC-MS analysis.

Results

The authors report % recovery of applied ^{14}C :

Day	Artificial Sunlight		Natural Sunlight		Control	
	Artificial Sunlight	Natural Sunlight Tracking	Natural Sunlight Non-tracking	Control Art.	Control Natural	
0	-----97.4-----					
6	91.0	80.6	77.9	92.6	93.3	
12	94.9	73.9	72.8	95.7	94.3	
24	77.5	57.7	64.8	90.4	93.4	
48	66.9	51.9	54.9	89.4	90.7	

Zone 1 of the TLC plates accounted for the majority of the extracted ^{14}C and was confirmed as being SD 43775 (fenvalerate).

The degradation products*, SD 47117 and SD 44607 were the major degradation products found in the soil, accounting for 1.9% to 6.1% and 1.0% to 7.8% of the applied ^{14}C when exposed to artificial and natural sunlight, respectively. SD 10944, SD 58086, SD 993 and SD 54597 were reported as minor

* See Figure 1 for structures and nomenclature.

photodegradation products. See Registrant's Tables 15 and 16.

The authors concluded that the rate of SD 43775 degradation followed pseudo first order kinetics for the first 12 days of the exposure:

Exposure Period	Reported Half-lives (days)			
	Sunlight		Control	
	Artificial	Natural	Artificial	Natural
0-12 days	12	6	53	33
12-48 days	-----13 to 28-----		130	95

Conclusions

EAB regression analysis of the submitted data calculates the following half-lives:

Exposure	Half-life (days)	r ²
Artificial sunlight		
Exposed	31	.9295
Dark Control	194	.8969
Natural sunlight		
Exposed-tracking	15	.9753
Exposed-non-tracking	23	.9699
Dark Control	144	.9957

From the above calculations, EAB concludes that (racemic) Fenvalerate will photodegrade on soil surfaces via natural sunlight with an initial half-life of 15 to 23 days.

This study provides additional information on the photodegradation of (racemic) fenvalerate on soil surface. Previous review (1/16/79) indicated that fenvalerate did not readily photodegrade to non-volatile compounds on the soil surface. In that study, the amide, SD 47114, was identified as the major photoproduct in both the exposed and "dark" controls.

Note: In the study described in Section 3.2.2, above, ¹⁴C₆-(SS)-fenvalerate degraded with reported half-lives of 2, 6, and 18 days on light clay, sandy clay loam, and sandy loam soil, respectively. CONH₂-fenvalerate (SD-47114) was found to be the major degradation product. However, insufficient data were presented for EAB to confirm these half-lives by EAB regression analysis.

3.2.7 Aerobic and Anaerobic Soil Metabolism of ¹⁴C-Chloro-phenyl-SD 43775. P. W. Lee. Report No. TIR-106-79.

This study has been reviewed by EAB previously 9/28/81 and was found acceptable. [redacted] fenvalerate degrades in soil under aerobic and anaerobic conditions (with little difference in the results of each).

4.0 CONCLUSIONS

4.1 Data submitted and reviewed [redacted]

To address this issue, it is recommended the registrant conduct (1) an aerobic soil metabolism study using typical cotton soil and radiolabeled a. i. and (2) field dissipation studies in three different cotton growing areas using the formulation.

4.2 [redacted]

We need a technical presentation by the registrant that would explain the relevant details and allow us to ask questions.

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Manufacturing process

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