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Date Out EFB: NOV 19 1980

To: Product Manager 17 Gee
TS-767

PROPRIETARY

From: Dr. Willa Garner Samuel M. Creeger (Acting Chief)
Chief, Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 201-401

Chemical: Pydrin

Type Product: Insecticide

Product Name: Pydrin

Company Name: Shell

Submission Purpose: For use on cotton

ZBB Code: other

ACTION CODE: 436

Date in: 9/3/80

EFB # 603

Date Completed: NOV 19 1980

Time (days) 18

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

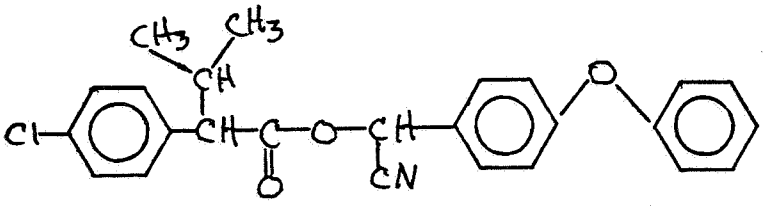
_____ Toxicology Branch

1. Introduction

Chemical Name and Type Pesticide: pydrin [cyano(3-phenoxypheny) methyl-4-chloro-alpha-(1-methylethyl) benzene acetate], 30% a.i., Insecticide.

Trade Name: PYDRIN Insecticide 2.4 EC, SD 43775

Structure



This is a submission of recently completed data that was cited as being required in a previous review (9/4/80).

2. Directions for Use

Not applicable.

3. Discussion of Data

3.1 HYDROLYSIS

Hydrolytic Stability of PYDRIN 2.4 EC Insecticide, K.S. Williams, Section A, p. 00002, Acc. #243109.

Experimental Procedure

Aliquots of SD 43775-41-5 were added to pH 5, 7, and 9 buffers to give a final emulsion concentration of about 0.05 lb a.i./gal. Incubation was in a water bath at 38 °C. At sampling times (zero, 18 1/2 hours, and 93 1/2 hours), a 1.0 ml aliquot was removed and diluted to 10 ml with methanol before being analyzed by LC.

Results

The insecticide did not degrade under these conditions.

Conclusions

PYDRIN is stable to hydrolysis. The study satisfies this EC data requirement.

3.2 EFFECTS OF PESTICIDES ON MICROBES

3.2.1 Determination of the antimicrobial activities of SD 43775 and SD 42049, S.C. Stackhouse, TIR-22-101-79, Tab 1, p. 00006, Acc. #243109.

Experimental Procedure

The antimicrobial activities of technical, analytical, and formulated batches of SD 43775 and SD 42049 were determined by inoculation of 12 bacterial species over 0.1, 1, 10, 100, and 100 microgram quantities of test compound spotted on the surface of tryptic soy agar plates. The cultures tested were:

Escherichia coli B (ATCC #11303)
Salmonella typhimurium (ATCC #7823)
Staphylococcus aureus (ATCC #13709)
Micrococcus flavus
Streptococcus fecalis (ATCC #19433)
Bacillus polymyxa (ATCC #842)
Proteus vulgaris
Proteus mirabilis (ATCC #9921)
Enterobacter aerogenes (ATCC #13048)
Alcaligenes eutrophus (ATCC #17697)
Pseudomonas aerugenosa
Aerobacter aerogenes

Results

At 1000 ug most test species grew right up to but not under droplets of SD 43775 (PYDRIN). Little or no inhibition was observed at lower concentrations.

Conclusion

SD 43775 did not inhibit growth of 12 bacterial test species. It should be noted that most of these bacteria are not normal, degradative soil inhabitants.

3.2.2 Impact of Commerical Shell Pesticides on Microorganisms in the Soil. Part III-Effect of Compounds on the Population of Microorganisms and the O_2/CO_2 Exchange in Treated Soil; Rader, Love, and Chai; TIR-22-112-77, p. 00011, Acc. #243109.

Experimental Procedure

Unsterilized field soil (Hanford sandyloam; Modesto, CA) was used at a soil moisture content of 6.0% (field capacity of 10.8%), a pH of 5.49, and contained 0.7% organic carbon. Twelve Shell pesticides were tested, with SD 43775 (PYDRIN) being at a 1X field dosage/A of 0.2 lb.

Three types of media were used to isolate microorganisms from the Hanford soil: soil extract agar was used for bacteria, peptone-dextrose rose bengal agar was used for fungi, and starch casein agar for Actinomycetes. Determination of O_2/CO_2 exchange in treated soil and in the presence of microorganisms and test pesticides was made with a Gilson Differential Respirometer.

Results

There was a correlation betwen the numbers of bacteria and fungi and the uptake of O_2 by these organisms in the soil, that is, the larger the numbers of these microbes, the greater the uptake of O_2. Actinomycetes in high numbers appear to result in negative relation with O_2 uptake by microorganisms in the soil. SD 43775 (PYDRIN) had no residual (adverse) effect on soil microorganisms.

Conclusions

Neither O_2 uptake nor microbial populations (bacteria and fungi) were adversely affected by the insecticide PYRDIN.

3.2.3 Impact of Commercial Shell Pesticide on Mircoorganisms in the Soil. Part IV-The effect of the compounds on Soil Nitification, W.E. Rader, TIR-22-112-77, 00035, Tab #3 Acc. #243109.

Experimental Procedure

Hanford sandy loam soil was used in the study. The bacteria tested were: Nitrosomonas europaea (ATCC #19718), Pseudomonas denitrificans (ATCC #13867), Nitrobacter agilis (ATCC #14123), and Nitrobacter sp. isolated from soil. Treated soil was kept at 80% °F between treating and sampling. Ammonia was determined by the amylose-cadmium iodide method as modified by Miller. Nitrate in soil was determined by the aluminium sulfate solution extration procedure. Nitrite was determined by Griess-Ilorvay reaction. Toxicity tests against Nitrobacter sp. were made using a sodium nitrite and salts solution containing 10, 100, and 1000 ppm of the pesticide. Bacteriastatic tests against Pseudomonas denitrificans using treated Emerson's broth media.

Results

After 4 weeks incubation, there was no inhibition of ammonia to nitrite oxidation by Nitrosomonas at 1X and 4X field dosage rate of SD 43775 (PYDRIN). Similarly, nitrite to nitrate formation was not inhibited by Nitrobacter sp. when 10, 100, and 1000 pp of PYDRIN was tested.

Conclusion

SD 43775 did not inhibit nitrification even when used at higher-than-field dosage rates.

3.2.4 The Effects of Shell Pesticides on Protein Decomposition, W.E. Rader, TIR-51-108-79, p. 00048, Tab #4, Acc. # 243109.

Experimental Procedure

The method of Ladd and Butler was used to assay the effects of 12 pesticides on the proteolytic enzyme activities in treated soil. The soil proteases were assayed by the release of tryosine from sodium caseinate in treated soil. Field dosages were at 1X and 4X and incubation was at 27 °C for 0, 4, 8, and 12 weeks. Oakdale loamy sand (California) was used.

Results

The 12 pesticides (incuding PYDRIN) showed no inhibitory effect on the soil proteases.

Conclusions

The protease that releases tyrosine from sodium caseinate was not inbibited by PYRDIN at 1X and 4X field dosage.

3.2.5 The Effect of Shell Pesticides on Soil Phosphatase Activity, W.E. Rader, TIR-51-110-79, p. 00053, tab #5, Acc. #243109.

Experimental Procedure

Oakdale loamy sand was used that had a moisture content 75% of field capacity (6.73%), a pH of 7.3, and contained 1.06% organic carbon. Field dosages were at 1X and 4X and incubation was 27 °C for 0, 2, 4, 8, and 12 weeks. Phosphatase in the soil was analyzed by the method of Tabatabai and Bremner.

Results

None of the pesticides produced a decrease in soil phosphatase activity.

Conclusion

SD 43775 did not inhibit phosphatase activity in soil after 8 weeks incubation.

3.2.6 The Effects of Shell Pesticides on Cellulose Decomposition, W.E. Rader and I. G. Blake, TIR-51-111-79, p. 00058, Tab #6, Acc. #243109.

Experimental Procedure

Eleven pesticides were tested for inhibition (decrease of CO_2 evalution) of cellulolytic enzyme activity in an in vitro test using Trichoderma longibrachiatum to degrade cellulose. On aliquot from a standardized spore suspension was added to inorganic salts and cellulose (12%) medium in a biometer flask. Pesticides were added to give 0.1, 1.0, 10.0, and 100 ppm. Flasks were incubated at 25 °C in the dark and envolved CO_2 was determined at 1, 3, and 7 days.

Results

Seven of the pesticides (including PYDRIN) did not produce an in vitro dosage response inhibition of CO_2 evolution; the other three pesticides did.

Conclusion

SD 43775 did not inhibit CO_2 evolution in an in vitro test.

3.2.7 The Effects of SD 43775 on Activated Sludge Metabolism, W.E. Rader and I.G. Blake, TIR-51-112-79, p. 00063, Tab #7, Acc. #243109.

Experimental Procedure

One liter of synthetic sewage medium was added to the aerobic sludge digestion unit (a specially prepared flask). Acetone solutions of the labeled (^{14}C in chlorophenyl position) and unlabeled SD 43775 to give 0.1, 1.0, 10.0, and 100 ppm were combined with activated sludge in the flask. Sampling was at zero time and after 23 hours, at which time the sludge, effluent, CO_2 trap, and ethylene glycol trap were sampled. Fresh sewage and pesticide were added to sludge, aerated for another 23 hours, and the samplings repeated. Analyses included viable bacterial counts, suspended solids, turbidity, total ^{14}C, and pesticide content.

Results

Total suspended solids and volatile suspended solids indicated good flocculation of the biosludge containing the test compound, as well as a slight increase in the biomass at the 100 ppm level. There was also no evidence of toxicity toward bacterial growth at this level. At the 0.1 ppm level, 3% of the label was trapped as CO_2, 2% at the 1.0 ppm level, and further decreaes at the 10.0 and 100 ppm levels. Turbidity measurements showed that most of the bacteria flocced and settled in 30 minutes after each 23 hour digestion period. Observations of the protozoa in the activated sludge made at the end of each incubation period showed no difference in numbers or activity at the pesticide levels tested.

Conclusion

SD 43775 did not inhibit the microbial flora or the operation of an in vitro activated sludge system.

3.2.8 Metabolism of SD 43775 by Enrichment Cultures Initiated from Freshly Collected and Pretreated Sandy Loam Soil, S.C. Stackhouse, TIR-22-120-79, p. 00074, TAB #8, Acc. #243109.

Experimental Procedure

Minimal salts plus SD 43775 (MS + P) and minimal salts plus glucose plus SD 43775 (MS + G + P) enrichment cultures initiated from freshly collected and pretreated Hanford sandy loam soil were tested for their ability to metabolize SD 43775 (fresh soil enrichment cultures) or ^{14}C-SD 43775 (treated soil enrichment cultures) over a period of 30 days. At 0, 7, 15 and 30 days cultures were sonicated and extracted with methanol. Percent SD 43775 was determined by liquid chromatography (LC). In the radiolabeled study methanol fractions were extracted with chloroform, dried and concentrated for analyses by liquid scintillation counting (LSC), thin layer chromatography (TLC) and autoradiography. Production of $^{14}C\text{-}CO_2$ was monitored by periodic LSC of samples from the KOH traps of biometer flasks containing the enrichment cultures.

Results

In LC and TLC/LSC studies, SD 43775 levels similar for both controls and enrichment cultures, indicating no detectable metabolism of the test compound. Biometer flask studies, however, indicated that a low level of metabolism of ^{14}C-SD 43775 occurred in the soil enrichment cultures. $^{14}C\text{-}CO^2$ produced by the biometer flask cultures amounted to only 0.6 to 0.9% of the radioactivity incorporated into the test media; levels found in the respective sterile media controls were 5 to 12 times lower.

Conclusion

SD 43775 underwent some metabolism in all biometer flasks, although slowly in the in vitro system.

All of the microbial studies evaluated above satisfy this EC data requirement.

3.3 SOIL FIELD DISSIPATION

3.3.1 1979-Dissipation of SD 43775 In Undisturbed Soil Following 15 Ground Spray applications of SD 43775 to cotton; An Alabama Study; F.R. Gilliland; Contractor: Agricon, Inc; p. 00108, Tab #; Acc. #243109.

Experimental Procedure

Sandy loam soil (0.62% O.M.) received 15 ground spray applications of PYDRIN 2.4 EC at a rate of 0.2 lb a.i./A. Sampling consisted of 0-3, 3-6, and 6-9 inch soil cores taken 0, 15, 21, 30, 45, 90, and 180 days after last treatment. Analysis was by GLC.

Results

At almost all sampling times, the highest residues (0.27 to 0.03 pm) in the 0-3 inch soil cores; the 180 day samples showed undetectable residues at all soil levels. The soil cores from the 0, 15, and 21 day samplings showed residues at 3-6 inches ranging from 0.02 to 0.08 ppm; at 6-9 inches it was 0.02 ppm or less. The 30, 45, and 90 day samplings showed no detectable residues below 3 inches. The half-life of SD 43775 was concluded to be 54 days.

Conclusions

Dissipation of SD 43775 in Alabama soil was confined mainly to the top 3 inches of soil. Pydrin was relatively short-lived (T 1/2 = 54 days).

3.3.2 1979 - Dissipation of SD 43775 In Undisturbed Soil Following Fifteen Applications of SD 43775 to Cotton, An Arizona Study; G.F. Barber; Contrator: Az-Tech Ag. Specialist, Inc.; TIR-24-140-79; p. 00122; Tab 2; Acc. # 243109.

Experimental Procedure

Sandy loam soil (less than 1.0% O.M.) received 15 aerial applications of PYDRIN 2.4 Ec (SD 43775) at a rate of 0.2 lb/A. Sampling consisted of 0-4, 4-8, and 8-12 inch soil cores taken 0, 14, 21, 30, 47, 80, and 172 days after last teatment. Analysis was by GLC.

Results

At all sampling times, the highest residues (0.19 to 0.04 ppm) were found in the 0-4 inch soil cores. The 4-8 inch layer showed residues of <0.01, 0.02, and 0.05 ppm after 0, 14, and 21 days, respectively. The 30, 47, 80, and 172 day samples, at 4-8 inch layer had residues ranging from 0.02 to <0.01 ppm. These same samples had no detectable residues at the 8-12 inch layer. Half-life was found to be 25 days.

Conclusion

Dissipation of SD 43775 was mainly in 0-4 inch layer and was degraded fairly rapidly (25 day half-live). Residues remained in 0-4 inch layer at 172 days and were not identified.

3.3.3 Dissipation of SD 43775 In Undisturbed Soil Receiving Fifteen Ground Spray Application of SD 43775 To Cotton, a Louisiana Study, C.K. Huston, Contractor: L.F. Bewick, TIR-24-391-78, p. 00153, Tab #3, Acc. #243109.

Experimental Procedure

Gallion silt loam was treated at the rate of 0.2 lb/A of 2.4 EC formulation. Sampling consisted of 12-inch soil cored cut into 0-3, 3-6 and 6-12 inch sections on 0, 15, 21, 30, 45, 91, and 180 days after last treatment. Analysis was by GLC.

Results

Sample	Residues		
	0-3	3-6	6-12 inches
0	0.93	0.1	0.07
15	1.0	0.1	0.13
21	0.87	0.07	0.06
30	0.58	0.02	0.01
45	0.97	0.02	0.02
91	0.26	0.03	<0.01
180	0.23	<0.01	<0.01

Half-life was determined to be 54 days.

Conclusions

Dissipation was mainly in the 0-3 inch sections and contained fairly high residues (0.23 ppm) even after 180 days that were not identified.

3.3.4 1978 - Residue Data SD 43775 In Undisturbed Soil Receiving 5, 10, or 15 Ground Spray applications of SD 43775 to cotton, an Oklahama Study; C.K. Huston; TIR-24-381-78-B; p. 00164; Tab #4; Acc. 243109.

Experimental Procedure

Clay loam soil (1.5% O.M.) was treated with 0.2 lb/A of 2.4 EC formulation. Soil from 0-3", 3-6", and 6-12" depths were sampled and analyzed by GLC after 0, 15, 22, 33, 47, 92, and 183 days.

Results

	Residues		
Samples	0-3	3-6	6-12 inches
0	0.63	<0.01	<0.01
15	<0.01	<0.01	<0.01
22	0.22	<0.01	<0.01
33	0.34	<0.01	<0.01
47	0.28	0.01	0.02
92	0.08	<0.01	<0.01
183	0.01	<0.01	<0.01

Half-life was determined to be 34 days

Conclusions

Dissipation was essentially all in the 0-3 "layer. After 183 days, residues were down to negligible or undectectable levels in all sections.

These four soil dissipation studies essentially satisfy the EC data requirements for this parameter, however, certain questions regarding analytical procedure remain. The protocol indicated that GLC analysis was used to quantify the amount of parent compound (SD 43775) present in acetone/hexane extract of the sample. The residue figures given, therefore, would seem to be only for SD 43775 (parent). Several questions must be addressed on this point:

1. Why was only the parent compound analyzed for ?

2. Are the residues given only for parent compound ?

3. Are degradates present in the soil cores that are being missed ?

4. Why wasn't TLC and HPLC used to identify and quantify degradates ?

3.4 LEACHING

Leaching Study of SD 43775 By Soil Column Chromatography, P.W. Lee, TIR-22-103-79, p. 00179, Section D, Acc. #243109.

Experimental Procedure

The soils studied were Tujunga agricultural sand, Hanford sandy loam, Commerce loam, and Catlin silty loam. SD 43775 was carbon-14-labeled in the chlorophenyl-ring position. Columns were 6x30 cm, treated soil was in top 3 cm, eluted with 20 acre-inches of water, and involved freshly treated soil and aerobically aged (30 days) soil. The aged, treated soil (sandy loam) was placed on the column and eluted with 0.5 acre-inch of water per day for 45 days. The elutions were analyzed by LSC and TLC.

Results

Distribution of Radioactivity

Fraction	Sand	Sandy Loam	Commerce Loam	Silty Loam	Aged Sandy Loam
0-3 cm	88.8%	105.6%	115.6%	84.4%	91.8%
3-6	7.6	3.5	0.4	3.6	3.3
6-30	2.9	5.3	2.9	5.9	3.1

Two degradates were recovered from the top 3 cm of the aged sandy loam soil: SD 44064, benzeneacetic acid, 4-chloro-alpha-(1-methylethyl) and SD 48838, benzeneacetic acid, 4-chloro-alpha-(1-methylethyl), cyano-(3-phenoxy-4-hydroxyphenyl) methylester.

Conclusions

SD 43775 showed very low mobility in 4 soil types. The study satisfies this EC data requirement.

4. Executive Summary and Conclusions

PYDRIN (SD 43775) was found to be stable to hydrolysis, did not inhibit microbial populations in soil, O_2 uptake, nitrification, protein degradation, phosphatase activity, cellulose decomposition, nor an *in vitro* activated sludge system. In field dissipation, the pesticide residues were confined to 3-4 inch layer with a half-life of 1-2 months; soil column leaching indicated pesticide immobility.

5. Recommendations

The studies on hydrolysis, effects on microbes, soil field dissipation, and leaching that were just reviewed are acceptable, but certain questions regarding analytical procedure remain. The protocol (Soil dissipation) indicates that GLC analysis was used to quantify the amount of parent compound (SD 43775) present in acetone/hexane extract of the sample. The residue figures given, would seem to be only for SD 43775 (parent). Several questions must be addressed on this point:

1. Why was only the parent compound analyzed for ?

2. Are the residues given only for parent compound ?

3. Are there degradates present in the soil cores that are being missed ?

4. Why wasn't TLC and HPLC used to identify and quantify degradates ?

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