Meeting
7/23/75

EEE BRANCH REVIEW

DATE: IN _____ OUT _____ IN 4/24/75 OUT 6/10/75 IN _____ OUT _____

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE XXXXXX. NO. 352-GTA

PETITION OR EXP. PERMIT NO. _____

DATE DIV. RECEIVED 1-13-75

DATE OF SUBMISSION 1-10-75

DATE SUBMISSION ACCEPTED _____

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

PRODUCT MGR. NO. 24 Jacoby

PRODUCT NAME(S) DuPont Krenite Brush Control Agent

COMPANY NAME E.I. DuPont

SUBMISSION PURPOSE New Registration

CHEMICAL & FORMULATION Ammonium ethyl carbamoylphosponate
4lbs. active per gallon

1 Conclusions

1.1 The analytical methodology submitted to determine "Krenite" residues in soil is adequate; however the procedure for determining the degradation products, previously requested, is still needed. Further, the major degradation product (X) must be identified.

1.2 Is the major product carbamoylphosphonic acid (CPA) or the unidentified soil product (X). There appears to be a discrepency on this point, figure #1 of exhibit #3 shows "X" as greater but the summarizing statement of exhibit #7 states CPA is greater. Clarification is needed on this point.

1.3 The basic environmental studies have been submitted to assess hazard on non-crop sites. Additional environmental chemistry data will be needed for application to other than non-crop areas.

2 Introduction

1.1 See previous review dated 9/25/73 for 352 Exp.

2.2 Percent active - 41% for this product (4 lb ai/gallon).

2.3 Uses - As a herbicide for brush control.

3 Directions For Use

3.1 For control and growth suppression of blackberry, --- make a single foliar application using 1.5 to 3 gallons of 'Krenite' per acre" (this is equivalent to 6-12 lb ai/acre) during the 2 month period prior to full leaf coloration. Product application is limited to [illegible] areas by either air or ground equipment: use ground equipment on ditch banks; use 10-40 gallons of spray per acre with aerial equipment. Add a nonionic surfactant such as DuPont Surfactant WK at 1qt/100gal spray.

4. Discussion of Data

4.1 Analytical methods

4.1.1 Flame Photometric GC (Exhibit 8) - The procedure for active ingredient is satisfactory. Recoveries from soil spiked to 0.1-4.0 ppm were 90-103%; in water at the same level, 96%. The ai was extracted with dilute ammonium carbonate (100°C); after 'clean-up' a silyl derivative was prepared and chromatographed on 30% OV-101, the column was programed between 100-260° at 25°C/min..

4.1.2 Using the techniques of TLC and TLC-electrophoresis, two degradation products were detected. One of these products,

carbamoyl phosphoric acid (CPA), was also found in the hydrolysis study.* The second product (X) has not been identified. Soil degradation of ai results in an X-CPA ratio of about 2 to 1.

All of the CPA is water soluble. However, only about 1/10th of the formed "X" dissolves in water, the remaining portion requires alkaline extractions (pH 10). This released the bound residues.

A second unknown (X_2) is recovered from the soil in much smaller amount which is thought to probably be reincorporated "^{14}C".

4.2 Other

4.2.1 Soil Property Data

Soil	Sand	Silt	Clay	O.M	pH
1	66	22	12	3.9	6.5
2	21	62	17	2.8	6.4
3	5	64	31	4.0	5.0
4	99	0	0	1.0	6.4

Soil 1, Fallsington sandy loam, Glasgow, Delaware
Soil 2, Keyport silt loam, Newark, Delaware
Soil 3, Flanagan silt loam, Rochelle, Illinois
Soil 4, Leon Immokalee fine sand, Brandenton, Florida

4.2.2 Reported Degradation Products and Metabolites.

Soil - Carbamoylphosphonic acid (CPA)
A major unidentified product (X_1)
A minor unidentified product (X_2)

Water - CPA only.

Photolytic - none; very little degradation.

Metabolites - None.

4.3 Degradation and Persistence Studies

4.3.1 Aerobic - See review of 9/73.

4.3.2 Anaerobic Exhibit 3

Except for the anaerobic condition, under nitrogen, the data of the new study and the previous study was similarly obtained.

* Identification was by an NMR procedure, previously reviewed.

Residue Data From Aerobic and Anaerobic Studies (%)

Soil No.	Time in Months Aer.	+ Anaer	Total "14C" Recovered	Aqueous Extr.s Distilled	pH 10	Non-Extractables
2	1	1	4.2	40.8	47.3	8.3
1	1	1	6.6	29.0	57.8	8.4
2	2	-	4.0	40.7	51.0	7.9
1	2	-	6.5	29.0	59.0	8.3
2	1	2	3.9	40.9	46.8	9.1
1	1	2	6.3	28.6	55.7	9.3
2	3	-	3.6	40.9	45.1	9.5
1	3	-	6.0	28.2	58.9	9.4

Conclusions

There is no significant difference between the aerobic and anaerobic study and the resulting soil residues.

4.3.3 Bound Residues Exhibit 3 - Additional work was requested to determine the time required for maximum soil binding of ai. The greenhouse study (Table II) indicates plateauing of these residues between the 3rd and 6th week; binding approximates 5% on Keyport and 7% on Fallsington loam. The field study (Table VI) approximates these figures, 9% on Keyport and 4% on Immokalee Sand, the plateau occurring within six weeks. The above figures agree with the data [illegible] indicating about up to 76% of total 14C was lost from two field soils in 6 months, and 69% in 1 year in another. About 30% of the 14C remaining in soil at the end of 1 year, 10% of the applied, was in the soil organic components with the highest amount in the B-humus and next in a-humus.

4.3.4 ~~4/3/4~~ Hydrolysis (Exhibit 2) - In 5 ppm solutions parent was stable at pH2 and 9(<3% decomposition) at pH5 (½ life 10 days to CPA). In 7200 ppm <1% degradation in 4 weeks. No explanation given.

4.3.5 Photodegradation

No significant degradation.

4.3.6 Degradation by Microbes (Exhibit 3) - Effects of soil Microbes on DPX-1108. The data was obtained with biometer flasks; incubation was at 24°C (dark), for 90 days. Soil samples (50 gm) wetted to 70% of capacity, were spiked with either 4 or 20 ppm of "14C - labeled" ai.

Evolved "14C - Carbon Dioxide" (%)

Days	Keyport			Fallsington		
	Control	Treated		Control	Treated	
	4 ppm	4 ppm	20 ppm	4 ppm	4 ppm	20 ppm
10	2	18	15	0.5	12	13
20	3	24	20	1.5	20	20
40	7	45	29	4.0	32	31
80	16	72	51	7.0	47	50
90	17	75	55	8.0	48	53

Conclusion

The data indicates microbial degradation of the ai.

4.3.7 Effects on Microbes.

4.3.7.1 Evaluation of DPX-1108 on the Population of Soil Microbes (Exhibit 5)

The study was made with Fallsington, Flanagan and Immokalle soils. The study included untreated controls. Test samples (100 gm), wetted to 65% of capacity, were spiked to 10 ppm with ai and incubated at room temperature for 8 weeks. Replica flasks were sampled after 1,2,4, and 8 weeks. One gram 'aliquots' of the soils were added to sterile water (100ml). Suitable aliquots were then spotted on agar for propagule assay of fungi and bacteria.

Fungi Populations ($x.10^4$) per Gram of Dry Soil

Soil	Time in Weeks							
	1		2		4		8	
	Control	ai	Control	ai	Control	ai	Control	ai
Flanagan	9.3	10.1	12.3	13.2	10.4	9.9	9.3	8.0
Immokalle	7.3	7.9	5.7	6.3	7.1	7.5	3.3	2.6
Fallsington	2.8	3.2	2.2	2.9	0.6	2.0	0.9	0.7

Conclusion

No significant effect on fungi populations. Data for other microbial populations is similar.

4.3.7.2 Evaluation of DPX-1108 on Nitrifying Activity of Soil Bacteria (Exhibit 6)

Air dried Keyport and Fallsington samples (100 gm), wetted to 50% of capacity, received additions of fresh garden soil. After mixing and equilibration (2 weeks, dark, 35°C) the samples received additions of ammonia sulfate (200 ppm) to expedite nitrification, and spikes of the ai; Fallsington, 0.5 or 5.0 ppm, Keyport, 5.0 or 20 ppm. The study included untreated controls and samples treated with "N-Serve" (3.0 ppm), a commercial nitrification inhibitor.

All samples were incubated at 35°C for 5 weeks. During this time nitrate was regularly determined - the nitrate was extracted (aqueous) and potentiometrically determined against a series of similar soil samples of known nitrogen content.

Average Nitrate (Mg) per Sample (100 gm)

Soil Treatment	Days							
	Fallsington				Keyport			
	0	6	10	24	0	6	10	24*
N-Serve	4.8	15	15	12	19	27	28.0	33
Control	5.3	43	84	85	19	81	106	120
ai (0.5 ppm)	4.4	41	81	85	--	--	--	--
ai (5.0 ppm)	4.9	35	80	85	18	82	106	120
ai (20 ppm)	--	--	--	--	16	81	106	120

* Figures in this column are interpolated.

Conclusion - Nitrification activity of bacteria was not significantly effected.

4.1 Mobility Studies

4.4.1 Laboratory Leaching - Direct (Exhibit 4)

Keyport and Fallsington soils.

Columns, 2 inches by 10 inches in length, were packed with soil, "14C-labeled" ai was added to the top of the column and leaching (rate not given) was applied until 20 inches passed through the columns; Fallsington time 7 days, Keyport time 20 days.

Summary

Activity Recovered (%)

Soil Section	Keyport	Fallsington
0 - 2 inch	43.5	27.3
2 - 4	21.5	34.6
4 - 8	10.5	13.7
8 - 12	3.2	9.5
Total in Soil	78.7	85.1
in Water	4.4	9.3
Recovered	83.1	94.3

Conclusions

The data supports other studies indicating the ai does not have much tendency to leach.

4.4.2 Leaching; Degradation Products (Aged Study)(Exhibit 4)

Keyport and Fallsington soils.

Aging Procedure - Soil, wetted to 30-80% capacity, was spiked with "14C-labeled ai at 10 ppm (13 lb ai/acre, assuming 0-4 inch) and aged 30 days (21-30%).

Leaching - Columns 2" by 12" in length were packed with soil and then 100 gm of aged soil was added to the top of each column and leaching, 0.5 inches per day, was initiated for 45 days.

Activity in the elutriate was counted daily; 2 inch soil sections were assayed for "14C" at the end of the leaching test. Degradation products were not determined.

Activity Recovered (%)

Soil Section	Keyport	Fallsington
0 - 2 inch	49.6	37.7
2 - 4	22.0	34.8
4 - 8	5.8	11.3
8 - 12	3.9	6.1
Total in Soil	81.3	89.9
in leachate	2.0 or less	2.0 or less
Total Recovered	83.3	91.9

Conclusions

Although there are some procedural differences between this and the direct leaching study (4.41) the data indicates neither the ai or the degradation products will leach significantly -- and less leaching of the degradation products than of the ai.

4.4.3 Run-off (Exhibit 4)

Flats, 12 by 36 by 3 inches were sloped 12% (between 5-10 degrees). The ai application rate was 15 lb ai/acre and to the upper third of the plot. "Rain" was adjusted to 25-50 ml of run-off in the two hours. Fallsington soil was used in the test.

Activity Recovered (%) in Increments Along Flat

Soil Layer	0 - 12 inch	12 - 24 inch	24 - 36 inch
First inch	92.6%	--	--
Second inch	1.0	--	--
Third inch	0.2	--	--
Total	93.8%	2.08%	0.33%

Conclusion:

The ai shows no significant tendency to leach or "Run-off".

4.4.5 Field Leaching Study - The data has been resubmitted and agrees with other work showing the ai with relative little mobility.

4.4.7 Long Term Persistence (Exhibit 3)- Our September 1973 review requested additional work to determine the time for extractable "14C-Residues" to reach a 10% level. The data indicates on Fallsington CA 63 weeks, on Keyport CA 36 weeks.

The estimates are based on the greenhouse data of Table II, which shows total and unextractable "14C". Steady dissipation occured after the sixth week; decomposition rates per week 1.18% (Fallsington) and 1.57%(Keyport). Extractables on the 10th week were 73%(F) and 51%(K). The time to the 10% level were then 63 weeks [(73-10)/1.18 plus 10] and 36 weeks [(51-10)/1.57 plus 10].

4.5.8 Channel Catfish, Four Week Residue Study (Exhibit 7)

"Test A" - Static study without soil; ai 1.1 ppm, 85% degraded during the 4 week test.

"Test B" - The usual catfish study with water and soil containing aged ai.

Note: Complete degradation of ai in the aging step. No ai was found in either soil or water during the test - exposure was to CPA and the unidentified product (X). Exhibit 3 (Fig. 1) indicates the water solubility of both CPA and X in ratio of about 3 to 1.

Aged soil - Fallsington (22 lbs) was air dried, spiked with "14C-ai" at 15 ppm, wet to 50% of "MC" and maintained at 30-60%. Temperature was 21 ± 2°C and aging time 30 days.

Aquariums - Glass, 3x3x1.5 (ft).

Water - pH 6, adjusted with buffer, 140 liters.

Fish - Channel catfish (50), averaging 4.4 gm and 8.3 cm.

Aqueous Concentration of ai and unidentified 14C-activity as CPA(X) Tests A and B (ppm)

Week	Test A(1)		Test B(2)	
	ai	CPA(X)	ai	CPA(X)
0	1.10	0.00	0.0	0.01
1	1.02	0.08	0.0	0.19
2	0.66	0.44	0.0	0.24
3	0.46	0.64	0.0	0.31
4	0.16	0.94	0.0	0.37
Average	0.69	0.42	0.0	0.22

Fish Accumulation Factors in Viscera for CPA(X), from "Test-B"

Week	Residue (ppm)	CPA, Solution (ppm)	BF
0	0.00	0.00	--
1	0.30	0.19	1.6
2	0.34	0.24	1.4
3	0.28	0.31	0.9
4	0.30	0.37	0.8
Average	0.24	0.25	1.0

The activity in solution is CPA and an unidentified soil degradation product X; no ai is present.

The viscera factor(1) is about 3 times larger than the edible tissue factor.

In "Test-A" residues approximate those of "Test-B" but resulted from exposure to both ai and CPA(X); the combined concentration being about 1.0 ppm. Consequently the factor were small - viscera, 0.25; and edible tissue about 0.08.

Most of extractable tissue residues were polar(CA 95%); partitioning was with water and chloroform under ultrasonic conditions.

Conclusions

Krenite and its soil degradation products do not significantly accumulate in catfish. It is further noted that about 50% of these residues were eliminated in a two week withdrawal period.

5 Summary

5.1 The product is applied only to non-cropland areas which do not have rotational crops.

5.2 Neither the ai or its degradation products show significant mobility.

5.3 There is no indication that ai or its metabolites will accumulate in fish.

5.4 Brief data summary.

5.4.1 Persistence

In water; the ai decomposes totally at pH 5.0 with a half-life of about 1.5 weeks. However at pH7 and 9 the ai is stable.

In soil; Bound Residues (4.3.3), from 5-10% of the applied ai binds, depending on the soil. Extractable Residues (4.4.7). The ai half-life is shown to be about 2 week (attachimentII). Degradation products dissipate steadily to a 10% level in an estimated time of 8 to 14 months.

5.4.2 Photodegradation - An aqueous study (9/73) indicates photolysis to be a relative insignificant factor. A decline of about 2% was noted in 8 weeks.

5.4.3 Microbial Studies

(a) Effect of microbes on the ai; microbial degradation (4.3.6) occured readily with a half-life of the applied ai of about 3 months. Further, degradation occured equally well under anaerobic and aerobic conditions (4.3.2).

(b) Effect of ai on the microbes; no effect on nitrifying activity (4.3.7.2) or on the populations of soil microbes (4.3.7.1), or on carbon dioxide evolution (4.3.6).

5.4.4 Residues in Rotational Crops - The product is intended for non-cropland areas, therefore, data are not needed.

5.4.5 Fish accumulation, factor in the viscera of catfish (CA 1), is not significant.

6/26/75

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