

EPA File Symbol 241-EG1

PP 4FL496 Submitted 5-1-74 Filed 5-23-74

American Cyanamid Co.

I. INTRODUCTION

*reviewed 2/24/74
10/16/74*

Applicant proposes registration of the above new insecticidal chemical for use against corn rootworms and wireworms with proposed negligible residue tolerance of 0.05 ppm of O, O-diethyl-S-t-butylthiomethylphosphorodithioate and its cholinesterase inhibiting metabolites in or on corn fodder, forage, and grain. Proposed product name is Counter 15G Soil Insecticide.

Applicant intends to replace phorate (O,O-diethyl S-[(ethylthio) methyl] phosphorodithioate with Counter. Note that Counter is t-butylthio while phorate is ethylthio.

2. DIRECTIONS FOR USE

Field Corn

Apply 5.0-6.5 lbs (12.0-15.6 oz a.i.) per acre (40 inch rows) or 6-8 ozs per 1000 feet of 20 inch rows (minimum) [6-8 oz/1000 row feet is about 23-31 oz a.i./A]

Apply at planting time in 7" band over the row directly behind planter shoe or place directly in seed furrow behind planter shoe. When applied in seed furrow do not use green forage or cut for silage prior to 130 days after planting.

This product is toxic to fish, birds and other wildlife

3. DISCUSSION OF DATA

3.0 Metabolism of CL 92100 in Soil (Section D-1 Exhibit III)

CL 92100 radiolabeled in methylene portion with ^{14}C was used to treat sandy loam (sand-silt-clay 68-24-8, pH 5.1, organic matter 3.6%) and Wisconsin silt loam (sand-silt-clay 24-56-20, pH 6.7, organic matter 5.2%). Sandy loam soil tested outside, silt loam tested in greenhouse Sandy loam treated at rate of about 1 pound (of product or active ingredient: unspecified) and silt loam treated at unspecified dose Soils were extracted 3x by acetone: methanol with 2 ml per gram of soil. Unextracted ^{14}C assayed by combustion. Sweet corn was grown in treated silt loam in greenhouse during study.

Results

Total ^{14}C (extractable and unextractable) in sandy loam declined fairly rapidly with half-life of about 3 months. Unextractable ^{14}C increased through 3 months to 14% of initial dose, then declined slightly to 10% of initial dose. Major portions of extractable and unextractable ^{14}C remained in top 4 inches of soil. Extractable ^{14}C decreased rapidly from 60% of initial dose in 0-2 inch core of 3 weeks to 15.7% of initial dose in 0-2 inch core at 3 months. In Wisconsin silt loam in green house 8.1% of initial ^{14}C was evolved as $^{14}\text{CO}_2$ and 0.3% as other volatile material.

Both outdoor sandy loam and greenhouse silt loam soil extracts were analyzed by TLC to determine relative distribution of ¹⁴C- bearing metabolites. The phosphorylated metabolites were CL 94301, CL 94320, CL 94302, and CL 94365 with CL 94301 predominant at shorter time intervals and CL 94320 predominant at longer time intervals (24 weeks). Less than 1% of total extractable ¹⁴C at 24 weeks is parent AC 92100. Silt loam showed same general distribution except at 10 weeks where CL 94320 was not predominant residue and CL 94301 was major residue.

When Wisconsin silt loam aged aerobically for 30 days, then anaerobically 30 days, polar metabolites at origin of TLC was 19.6%, CL 94320 was 28.5% and CL 99875 was 17%. CL 99875 is dephosphorylated methylated moiety, some of which was seen under the aerobic study.

Conclusions

AC 92100 degrades rapidly to CL 94320 through CL 92301 and also to CO₂. The halflife of AC 92100 - related compounds in sandy soil is 3 months. Dephosphorylation then methylation may occur during degradation but primary metabolites are parent compound with two sulfur oxidation states. Some possible oxygen analog and sulfur oxidation compounds found.

3.1 Field Soil Persistence of Counter Residues (Section D-2-C Exhibits X,XI,XII,XIII)

Field persistence samples were taken from 11 studies in 5 states. Two studies had zero day samples, another study had original sample at forty days and remainder of studies had samples at 100 + days. Soil samples were taken in the center of 7" treated band. Analysis by GLC method which measures total oxidative metabolites AC 92100, AC 94301; AC 94320, AC 94302 and AC 94365 as AC 94302. Dephosphorylated metabolites not determined. Soils were treated at 1.0 pounds active ingredient per acre.

Results

The two studies with zero-day samples had expected residues of about 6 ppm in top 3" soil. By day 40, residues were less than 1 ppm. Decline after forty days was less rapid. At five months (150 days) soil residue leveled out at about 0.2 ppm with significant residues occurring at 300 days in both 0-3" soil core and 3-6" soil core. The 3-6" cores of some studies showed residues which may be result of leaching.

An estimate of halflife would be one month for the oxidative metabolites, however not enough samples at less than forty days to define halflife more closely.

Two studies merit closer inspection. One study in Greeley Colorado showed 0.40 ppm and 0.16 ppm in 0-3" and 3-6" cores at 150 days and virtually the same but inverted at 309 days 0.15 ppm (0-3") and 0.40 ppm (3-6") on land that had been treated the previous year with phorate. In another study in Ames Iowa which was treated the previous year with Mocap (O-ethyl S,S-dipropyl phosphorodithioate), only one soil sample at 61 days showed detectable residue of 0.10 ppm, but at 40, 81, 100, and 139 days residues were below detectable level of 0.05 ppm.

It appears that previous treatment with similar chemical may predispose to rapid degradation, while in another soil this predisposition is not shown.

When soil samples (4) were analysed by another method for individual oxidative metabolites, the major metabolite found was AC 94301 which is the sulfoxide of parent AC 92100. This is similar to the degradation found in the soil metabolism study except that AC 94320 was not the major residue since the study was not long enough to show major degradation of AC 94301 to AC 94320. Since unextractable residues were not greatly significant in the soil metabolism study, it is not expected that unextractable residues occur to significant degree in the field persistence samples.

It should be noted that some of the field persistence studies included a layby treatment about 30 days after planting-time treatment.

It should also be noted that gas chromatograms of actual field samples from treated plots are not submitted. All chromatograms are from check soil (no treatment) for recovery studies. GC-grams from actual field-treated soil samples are needed.

3.2 Metabolism of ^{14}C -Counter in Sugar Beets (Section D-1 Exhibit IV)

Sugar beets were grown in greenhouse in Colorado sandy loam soil treated with about 6.1 pounds active ingredient per acre in-row band application rate. ^{14}C -methylene and deuterium label CL 92100 was used. Beets harvested at 4, 5, 8, 16 weeks and divided into root and foliage fraction. Analysis by ^{14}C counting and TLC of extracts (extracting solvent or procedure is not specified).

Results

1. In both foliage and roots of sugarbeets, the sulfoxide and sulfone of AC 92100 were major residues at 4 weeks, with some oxygen analog sulfoxide and sulfone. However at maturity, the relative distribution and amount of the metabolites decreased with concurrent increase in the dephosphorylated methylated metabolite 99875, t-butyl(methylsulfonyl) methyl sulfone. We note that plant metabolism degrades AC 92100 more completely than soil. Soil metabolism only to sulfoxide and sulfone while plants show oxygen analogs and dephosphorylated metabolites. Co-extracted sugars contained some radioactivity.

3.2.A Residues in soybeans as a followup crop grown under field conditions. (Book II, D-2, Exhibit-V)

Study I (Piper Kansas)

Treated June 19, 1973, corn disked in and soybeans planted July 9, 1973.

Soil - Silty Loam, 21% sand, 49% silt, 30% clay, 3.2% OM, pH 6.8

lbs A/A	Treatment Harvest	Planting Harvest	ppm	
0.98	78	58	.05	foliage
(7" band)	112	93	.05	"
	142		.05	"

Study II (Ames, Iowa)
treated June 7, 1973, 13 days later corn hoed out and soybeans planted
June 20, 1973.

Soil - 38.2% sand, 38.4% silt, 23.4% clay, 4.06 OM.

lbs A/A	Treatment to harves	Planting to harvest	ppm	
2	103	90	.05	whole plant
(7" band)	140	127	.05	grain

Study III (Ames, Iowa)
treated June 1, 1972, soybeans planted June 7, 1973.

Soil - same as study II

lbs A/A	Treatment to Harvest	Planting to Harvest	ppm	
2	462	90	.05	whole plant
(7" band)	511	140	.05	grain

All studies analyzed for total CL 92100 by method M-480 (flume ionization
GC with cesium bromide salt tip).

Conclusion

These data will support rotation of soybeans but addition studies are needed
for a more liberal use pattern.

3.3 Residues in Soybean as followup crop Section D-1 Exhibit V

Wisconsin silt loam soil used for growing sweet corn was also used for
soybeans. Soil treated at 6 lbs per acre (in-row concentration when
band applied), then 4 months later soybeans seeded. Methylene-¹⁴C-
AC 92100 was used. Soybean plants divided into pods, seeds, and
foliage Analysis by ¹⁴C-counting and by TLC.

Results

At maturity, ¹⁴C residues equivalent to AC 92100 were 11.7 ppm in foliage,
4.0 ppm in seed pods, and 4.3 ppm in seeds. Major metabolite found was
(99875), t-butyl (methylsulfonyl) methyl sulfone. When examined by TLC
for individual metabolites, the total amount of phosphorylated metabolites
was 0.21 ppm in foliage and 0.008 ppm in seeds at maturity (ppm equivalent
to AC 92100).

3.4 Soil Leaching Study (Section D-1-Exhibit VI)

Four soil types were studied for leaching of AC 92100. Additionally, one soil type studied using 30-day old treated soil to show leaching of AC 92100 metabolites.

Soil Type	Sand%	Silt%	Clay%	pH	OM%	CEC
Sand	96	4	1	4.9	0.26	1.6
Sandy loam	66	18	16	5.1	1.85	6.1
Silt loam	16	73	11	5.7	4.7	15.7
Clay loam	8	40	52	6.5	6.03	41.6

Soil columns 14 inches high were leached with 20 column inches of water in about 25 hours. It is assumed that methylene - ^{14}C -AC 92100 was used, but this is not stated in report. The equivalent field rate of 5 ml of stock solution is not described. Soil columns treated in 1.3-2.0 ppm range

Results

Less than 1.5% of applied ^{14}C found in leachate in agricultural sand, 1.1% from sandy loam, 0.5% from silt loam, 0.3% from clay loam. Of the initially applied ^{14}C , total recovery ranged from 56 to 88%, with 90 + % of recovered ^{14}C found in top quarter (3.5 inches) of soil column. Only in sand does ^{14}C appear to leach into second quarter of column.

When 30 day aged sandy loam is leached at the rate of $\frac{1}{2}$ inch of water per day for 45 days, ^{14}C is significantly leached into the second quarter of the column. Up to 17% of initial ^{14}C is found at 3.5-7.0 inches and 36% found in 0-3.5 inches, with 2.1% in leachate. The nature of the ^{14}C bearing moiety is not investigated.

It appears that metabolites or degradates of CL 92100 will leach more than parent. However this limited mobility of metabolites under stressful circumstances does not appear to be of great significance.

3.5 Hydrolysis and Photolysis (Section D-1 Exhibit VII)

Hydrolysis in sterile water at pH 5.7 and 9, photolysis - hydrolysis in pond water, photolysis of thin-film on glass, and photolysis on silica-gel studies were conducted

Hydrolysis in sterile water at pH 5, 7, 9 studied using methylene ^{14}C -AC 92100 using 4.62 ppm in water at temperature $20-25^\circ\text{C}$. Samples taken over 4 week period. AC 92100 is most stable at pH 9 with half-life of 8.5 days, with shorter half-lives at pH 7 and 5 (5.5 days and 4.5 days respectively). Formaldehyde was primary metabolite found at 4 weeks (70% at pH 5, 50% at pH 7, and 59% at pH 9) while second most abundant ^{14}C compound was parent. Traces of oxygen analog, parent sulfoxide and sulfone, and dephosphorylated methylated thiol compounds also found as less than 3%.

Photolysis-hydrolysis of AC 92100 in pond water
Pond water at pH 5.7 treated with 4.6 ppm
AC 92100 was exposed for 8 days natural

dark controls. Temperature range $24-40^\circ\text{C}$ and light intensity 3800-10200 foot candles. Significant difference between exposed and dark samples. Dark samples hydrolysed to formaldehyde which was somewhat lost by volatility. Parent compound degrades to 2.1% in dark and 0.1% in sunlight exposure in 8 days. In the exposed samples, traces of sulfone, oxygen analog sulfoxide and sulfone, were found but major amount 36% was parent sulfoxide. Hydrolysis was predominant activity in dark samples and photooxidation of parent to sulfoxide was major activity in exposed samples. The sulfoxide (from photooxidation) is not unstable by hydrolysis and therefore more persistent.

Photolysis of thin-film on glass resulted in lowered recoveries for exposed samples than for dark samples. Metabolites were phosphorylated series. Results of photolysis on silica gel were similar.

3.6. Rat Metabolism of AC 92100
(Section D-1 Exhibit VIII)

Methylene- ^{14}C -AC 92100 used to treat rats
No $^{14}\text{CO}_2$ found during 72 hours. Major
route (83%) was urine, minor route 3.5%
feces, tissue residues buildup then deplete
to less than 0.1 ppm. After 168 hours,
90% of dose has been recovered in urine
feces, tissues, and cage washes. Tissue
residues were 72% - 96% methylated
mercaptan metabolites.

3.7 Effects of AC 92100 on Microbial Activities (Section D-1 Exhibit IX)

Three Iowa soil types were studied

Soil	Sand%	Silt%	Clay%	pH	OC%
Clarion	39	39	22	5.7	2.77
Harps	24	43	33	7.0	4.16
Webster	29	45	26	6.3	3.78

The following microbial activities were studied: ammonium production, nitrification, carbon dioxide evolution, sulfur oxidation, cellulose decomposition.

Results

When tested at 1, 10, 50 and 100 ppm, no significant inhibitory effects were shown. In Harps soil, there was decrease of cellulose decomposition at 1 and 10 ppm but not at 50 or 100 ppm.

3.8 Kinetics of "Aged" ^{14}C -AC 92100 in a Synthetic Aquatic Ecosystem (Section D-1 Exhibit Xa)

Methylene ^{14}C -AC 92700 used to littleton Wisconsin silt loam soil (sand silt clay 24%, 56%, 20% pH 6.7, organic matter 5.2%) at rate approximately equivalent to 1.0 lb a.i./A and treated soil allowed to age 30 days. After ageing, treated soil mixed with 119 parts untreated soil, placed in 8 feet diameter pool to depth about 1 inch and 18 inches water added (2160 liters). There upon, 150 test organisms of each species were added to treated-soil pool plus check pool. Test organisms were bluegill sunfish weight 10 grams length 72 mm channel catfish weight 8.2 grams length 80 mm and crayfish weight 30 grams. Water, soil, fish and crayfish samples taken during exposure (35 days) and withdrawal (14 days). Relative distribution of ^{14}C between edible and non-edible portion examined, bluegill at day 10 and catfish at day 35. Distribution of ^{14}C during withdrawal not examined, therefore it cannot be determined whether ^{14}C is disaccumulated or translocated within fish. All fish samples were of edible portions only. Standard radioassay procedures were followed

Results

All bluegill sunfish were dead in treated pool at day 10, with first mortality occurring on day 4.

Water had concentration of ^{14}C of 0.14 ppb at day 1 which increased to 1.2 ppb at day 14 and remained relatively constant to day 35 with slight decline to 0.95 ppb.

The soil had a loss of about 60% of initial ^{14}C during 30 days ageing, leaving 41.6 ppb in soil at start of fish study. This concentration decreased to about 29.5 ppb at day 35. The chemical nature of the ^{14}C moiety in water and soil was not examined.

Bluegill sunfish contained 9.1 ppb in edible portions by day 3, increasing to 11 ppb at day 7, declined to 10 ppb at day 10 at which interval all bluegill sunfish had been killed by AC 92100 or its degradation (hydrolysis) products. Relative distribution of ^{14}C between edible and nonedible portions of bluegill showed 78 ppb in non edible portions (8 times concentration in edible portions and about 78 times concentration in water. Nature of ^{14}C moiety in edible or non edible portions not examined. Bioaccumulation factors from dead fish are not extremely reliable. It can be concluded that bioaccumulation in bluegill sunfish does not exceed 100 X although such concentration si or may be fatal.

Channel catfish showed maximum ^{14}C of 11.1 ppb at day 35 in edible portions and 30 ppb in nonedible portions (3 times the concentration in edible tissues) No reported mortality of catfish. Nature of ^{14}C moiety in edible or non-edible portions not examined. Total bioaccumulation in catfish (edible and nonedible) does not exceed approximately 50x.

Crayfish edible portions (tail muscle) had maximum ^{14}C of 4.3 ppb at day 7 with slight decline (and variation) to 3.1 ppb at day 35. Nonedible portions not examined for ^{14}C . Nature of ^{14}C in edible portions not examined. Total bioaccumulation in crayfish edible portions does not exceed 10x the concentration in water.

None of the test species accumulated ^{14}C to the extent found in soil (30 ppb) except nonedible portions of bluegill sunfish. Total biomass accumulated less than 1% of total initially applied to soil and less than 2% of the total ^{14}C available in the soil and water after ageing.

During withdrawal, concentration of ^{14}C in edible tissues of catfish and crayfish declined 63% and 55% respectively. Whether this decline was actually due to elimination from tissue or just transferred to nonanalysed fish tissues is not demonstrated. Disaccumulation or elimination is not proved.

AC 92100 (ug/l or ug/kg)					
Day	Soil	Water	Crayfish	Catfish	Bluegill
1	43.1	0.14	0.4	2.1	2.4
3	50.4	0.57	0.7	7.4	9.1
7	40.0	0.77	4.3	6.0	11.1
10	33.0	0.85	2.0	3.6	10.0
14	30.0	1.19	3.3	4.0	*
21	23.3	1.10	1.7	6.5	*
28	28.3	0.97	2.4	8.0	*
35	29.5	0.95	3.1	11.1	*
1 WD	-	-	3.5	8.5	*
3 WD	-	-	1.8	6.3	*
7 WD	-	-	1.8	6.1	*
10 WD	-	-	0.9	4.8	*
14 WD	-	-	1.4	4.1	*

* All bluegill killed by Day 10

Conclusions

^{14}C derived from AC 92100 does not bioaccumulate to significant degree in bluegill sunfish, channel catfish or crayfish over 35 days. Nature of accumulated ^{14}C not examined.

3.9 Accumulation and Persistence of Counter - Related Residues in Channel Catfish (Section D-1 Exhibit X 6)

Aged Wisconsin soil was extracted and aliquots of extract added to two fish tanks, one as single dose and other tank as smaller multiple doses. The manner in which the soil was extracted is not described. Tank #1 received 1.3 ppb as single dose to simulate sudden contamination and tank #2 received 0.18 ppb 6 times (total 1.08 ppb) over 7 days to imitate slow release by eroded soil. Channel catfish fingerlings exposed in tanks for 14 days then in untreated water for 21 days.

Results

In Tank #1 at 1.3 ppb, 25% of catfish died within two days. At this sample interval edible portions ^{14}C was 20 ppb but this declined throughout further exposure and withdrawal. However, even at 35 days after single 1.3 ppb treatment, edible portions contained 2.5 ppb and nonedible portions contained unknown amounts (not analysed).

In Tank #2, catfish did not although edible portions contained up to 17 ppb and 22 days after last multiple dose still contained 10.0 ppb of ^{14}C in edible portions and unknown amounts in nonedible tissues (not analysed). It is interesting to note almost no decline in ^{14}C in water of Tank #1 over 14 days and yet edible portion residue decline.

Conclusions

This ecosystem is an interesting variant. However, until further information is provided concerning the extraction procedure, we cannot conclude that the system is valid. If, as it appears, the extraction was conducted on a lab soil sample, the nature of the metabolites present in the soil would be important.

3.10 CL 92100 and Metabolites in Wildlife Tissues and Eggs (Section C-2 Exhibit VII)

Cornfields were treated with Counter 15G Various wildlife specimens were collected.

Results

Pheasant eggs from nest contained less than 0.01 ppm of CL 92100 and oxidative metabolites. Three mice trapped in fields showed 0.13, 0.18, and 0.22 ppm total residue. One grackle found dead contained 2.74 ppm. Fifteen other specimens of mice and birds had residues below level of sensitivity 0.05 ppm. Whole body samples only.

- 4.6 AC 92100 has hydrolysis half-life of less than 10 days at pH 5,7 and 9. Most stable at pH 9. Formaldehyde was primary hydrolysis product, greater than 50% at 4 weeks in all three pH's but parent was next most abundant material.
- 4.7 Photooxidation of parent compound to its sulfoxide is major photolysis reaction which occurs but sulfoxide is not too susceptible to hydrolysis and may be more persistent than parent.
- 4.8 When tested at 1,10,50, and 100 ppm no significant inhibitory effects were found in ammonium production, nitrification, carbon dioxide evolution, sulfur oxidation, cellulose decomposition.
- 4.9 All 150 bluegill sunfish were dead by day 10, when ^{14}C content of water reached about 1 g/l. Bioaccumulation factors in dead or dying bluegill were 10x in edible portions and 78x in nonedible portions. No plateau level reached since fish were dead.
- 4.10 Channel catfish showed maximum ^{14}C of 11x at day 35 in edible portions and 30x in nonedible tissue.

5. RECOMMENDATIONS

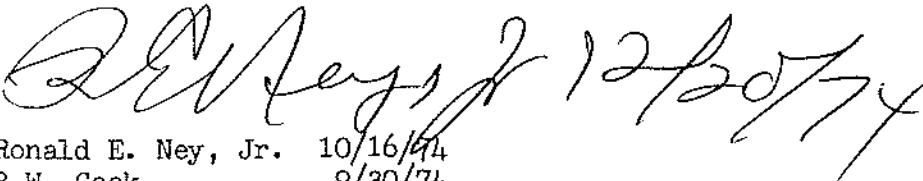
A. Object to registration

1. There must be a caution on the label such as "Do not rotate treated area for one year following application except for soybeans. Cover crops may be planted in treated area if plowed under and not grazed. Data as outline below are needed to continue registration.
1. Residue data on rotational crops are needed. A laboratory study using radiolabeled pesticide is recommended.
 - a. 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 a root crop, small grain and a vegetable crop: The root crop is required but crop crops in two other crop groupings may be used.
 - b. For crops rotated the following year after treatment, the pesticide is to be aged in the soil for one year. Use crops as above.
 - c. If significant residues are found then actual field studies using non-labeled pesticide will be needed. This data is to be obtained under actual agricultural practice.
 - d. If residues are found in rotational crops then labeling restrictions will be needed. This restriction will be a time interval from application to a time when rotational crops can be planted and not result in the uptake of illegal residues in the rotational crops. A restriction can be no longer than 18 months.
 - e. Cover crops can be rotated if label restrictions are such that the cover crop is plowed under and not grazed.

- f. 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 needed on the rotational crop. The rotational crop is to be grown under actual use conditions.

A complete review of the environmental chemistry data has not been made at this time. This is in connection with the fish accumulation study which will require further review.

Note: Pat Critchlow we are requesting criteria from C&ED


Ronald E. Ney, Jr. 10/16/74
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Environmental Chemistry Section
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j.t./11/14/74