114501
SHAUGHNESSEY NO.

6
REVIEW NO.

EEB BRANCH REVIEW

DATE: IN 10/22/82 OUT 1/21/83

FILE OR REG. NO. 264-GUE, 264-GUR

PETITION OR EXP. PERMIT NO.

DATE OF SUBMISSION 10/13/82

DATE RECEIVED BY HED 10/21/82

RD REQUESTED COMPLETION DATE 2/09/83

EEB ESTIMATED COMPLETION DATE 2/02/83

RD ACTION CODE/TYPE OF REVIEW 111/New Chemical

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

DATA ACCESSION NO (S).

PRODUCT MANAGER NO. J. Ellenberger (12)

PRODUCT NAME (S) LARVIN 75WP: 264-342

LARVIN 500: 264-341

COMPANY NAME Union Carbide

SUBMISSION PURPOSE Proposed Conditional Registration of field corn and sweet corn uses

SHAUGHNESSEY NO.	CHEMICAL, & FORMULATION	% A.I.

Environmental Safety Review
Fish and Wildlife

100.0 Pesticidal Use. Union Carbide Agricultural Products Company Inc. has requested an amendment to the registration of Larvin 75WP (EPA Reg No 264-342 and Larvin 500 (EPA Reg No 264-341) to allow use on field and sweet corn.

100.1 Application Methods/Directions

Specific use Directions for the two formulations of Larvin are the same. The proposed labels give the following use directions:

Field Corn

Foliage, silk, and ear feeders:

Refer to general use directions.

Insects feeding in plant whorl:

For best results use sprays of 10 gallons or more per acre applied by ground equipment using solid or hollow cone nozzles directed into the plant whorl.

Postemergence rescue treatments only:

For best results apply as a broadcast spray when cutworms are actively feeding. If banding use a minimum width of 10 inches over the row. To determine the amount of chemical to use per acre divide the band width by the row width and multiply by the appropriate broadcast rate.

Sweet Corn

Insects attacking silks and ears:

Apply at 1-7 day intervals starting when silks first appear and continuing until silks begin to dry or infestation potential ceases. Follow local recommendations for proper timing.

Whorl or foliage feeders:

Refer to general directions for use and specific directions under field corn.

100.2 Application Rates

Larvin 75 WP

Crop	Insect	Dosage/Acre lbs AI	lbs 75 WP
Field Corn	Armyworms European Corn Borer Western Bean Cutworm Corn earworm Cutworms	0.5 to 1.0	0.66 to 1.33
Sweet Corn	Corn Earworm European Corn Borer Armyworms Western Bean Cutworm	0.5 to 0.75	0.66 to 1.00

Larvin 500

Crop	Insect	Dosage/Acre lbs AI	Fl. oz
Field Corn	Armyworms European Corn Borer Western Bean Cutworm Corn earworm Cutworms	0.5 to 1.0	15.2 to 30.4
Sweet Corn	Corn Earworm European Corn Borer Armyworms Western Bean Cutworm	0.5 to 0.75	15.2 to 22.8

Larvin 75 WP

Field & Popcorn
Do not exceed 4.0 pounds of active ingredient per acre per season.

Sweet Corn

Do not exceed 7.4 pounds of active ingredient (10 pounds of 75 wp) per acre per season.

Lavin 500

Field & Popcorn

Do not make more than 4 applications per season

Sweet Corn

Do not make more than 10 applications per season

100.3 Precautionary Labeling

Environmental Hazards: Avoid direct applications to lakes, streams and ponds. Do not apply when weather conditions favor drift from area treated. To avoid toxicity to bees, do not apply when bees are actively foraging in areas to be treated.

Note: Above statement on Environmental Hazard was taken from the label proposed for cotton and soybean use. Approved label was not transmitted.

101.0 Chemical and Physical Properties

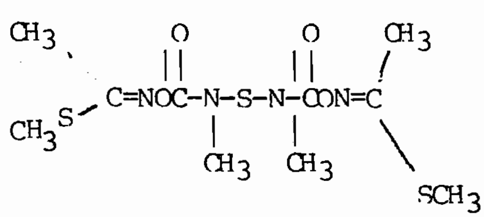
101.1 Chemical Name

Dimethyl N, N^{1}–[thiobis[(methylimino)carbonyloxy]']bis [ethanimiodothioate]

101.2 Common Name

Thiodicarb
Larvin™

101.3 Structural Formula



101.4 Molecular Weight

354.5

4

101.5 Physical State
color - white
odor - slightly sulfurous

101.6 Solubility
water - 35 ppm at 25°C
octanol/water partition coefficient
=1.65 (log P by reverse phare TLC technique)

102.0 Behavior in the Environment

The following information was presented in an EFB review on Thiodicarb date May 1, 1981.

Hydrolysis

In water, thiodicarb is relatively stable at pH 6 as indicated under the test conditions by only a 3% loss of the parent chemical over 9 days. However, aqueous hydrolysis occurs in alakaline and strongly acidic conditions and is most rapid under alkaline conditions. Half-lives of 8.6 and 0.9, days were obtained at pH 3 and 9, respectively. The major hydrolysis product of thiodicarb is methomyl. Methomyl oxime has also been identified as hydrolysis product. Methomyl is found to be stable at pH 3 and 6 but hydrolyzes at pH 9.

The study on stability of thiodicarb in lake, pond and well waters indicates that no ^{14}C- volatile residues are formed. Thiodicarb in ponds and well water degrades predominantly to methomyl thru cleavage on N-S bond and methomyl once formed is relatively stable. Only small amounts of methomyl oxime was detected in all samples. Methomyl methylol was detected in trace amounts.

Photo-Degradation

Thiodicarb photodegrades in aqueous solution, and more rapidly with acetone as sensitizer. The half-lives are 19 and 81 days, with and without acetone, respectively. Methomyl is the major product: minor products include the monosulfoxide, methomyl oxime, methomyl sulfoxide, and methomyl sulfoxide oxime (structures below in Figure 1). Photolysis of thiodicarb was also studied on the surface of soil. On soil, the initial photolysis product is methomyl; lesser amounts of methomyl oxime are formed and high volatile losses occur (28-83%). Reported half-lives range from 8 hours 7 days and >28 days for the three soils studied. The faster degradation rate occurred on the soil of the lighest texture and the only one with an acidic pH, i.e., the sandy loam.

Aerobic and Anaerobic Soil Metabolism

Thiodicarb degraded rapidly in soils under both aerobic and anaerobic conditions. Half-life values of thiodicarb were less than 1 week and about 1 week under aerobic and anaerobic conditions, respectively. The primary degradation product in both processes was identified as methomyl. Methomyl further degraded to CO_2 under aerobic conditions and to acetonitrile under anaerobic conditions.

The amount of methomyl oxime formed was highly variable, (2-25% of the applied radioactivity in the Texas soil, 0.1-3.2% in the other two soils). Physicochemical factors can produce the degradation to methomyl and methomyul oxime, but microbial and metabolism is responsible for the production of the volatile products, CO_2 and acetonitrile.

The half-life of thiodicarb in sterile soil is less than 8 days; methomyl is the major degradation product. This suggests that the first degradation step could be entirely due to physico-chemical processes. Further degradation to methomyl oxime occurs slowly (17% maximum over 62 days) and production of volatile products beyond methomyl is due in, part, to microbial action.

Effect of Microbes on Thiodicarb.

The impact of microbes on the degradation of thiodicarb was addressed (during the aerobic and anaerobic soil studies) under degradation in sterile vs non-sterile soils. In sterile soils thiodicarb did not degrade beyond methomyl except for some hydrolysis to methomyl oxime. In the non-sterile soil, degradation due to microbes occurs beyond methomyl oxime resulting in the formation of CO_2 and acetonitrile. The microbial activity is affected by decrease in temperature resulting in lower degradation rate.

Effect of Thiodicarb on Microbes

Thiodicarb at 1 and 10 ppm generally had no effect or slightly stimulated degradation of protein, starch, celloluse, and pectin in pasture and forest soils. The effect of thiodicarb on aerobic nitrogen fixation in pasture and forest soils are not conclusive: the effect varied from stimulatory to inhibitory over the course of study, and aerobic nitrogen fixation was low or undetectable in many control samples. The anaerobic nitrogen fixation was not affected by thiodicarb at 1 or 10 ppm had no prolonged effects on the nitrification in pasture or forest soil.

Mobility

Leaching and Adorption

Using TLC method, soils from different geographic regions were examined for leachability of thiodicarb and its metabolites. The TLC frontal Rf values for thiodicarb in different test soils ranged between 0.08 to 0.21. For the degradates, methomyl and methomyl oxime, Rf values were 0.9 and 0.8, respectively. Based on a classification system of relating mobility in soil to frontal Rf values, thiodicarb was rated under low mobility (class 2), whereas the metabolites were classified under the relatively high mobility group (class 5).

Absorption and desorption properties were evaluated on three of the soil types used in the above leaching studies. (California silt clay loam, Norfolk sandy loam and Texas sandy loam). The absorption coefficient K values calculated in these soils ranged between 0.6 to 1.34. After 3 hours of desorption, 64-84% desorption occurred. Degradation occurring during adsorption explains the low adsorption coefficient values determined the test soils and rapid release of the more mobile residues during desorption.

Field Dissipation

Field Dissipation in Soil

The half-life and dissipation rate of thiodicarb cannot be determined from the data because the extraction and analysis procedures and recovery data were not presented.

No soil characteristics were reported for any location nor were the size of the plots.

Because nothing is known about analytical procedures, used, it is not clear whether the residue levels reported include the residue levels of thiodicarb degradation products. Residue levels of 2.39, 0.20, and 1.36 ppm were found in one of the Texas control plots at 1, 3, and 7 days after treatment, respectively. This indicates either that some of the thiodicarb drifted onto the control plot or that the analytical recovery capabilities of the method were inadequate.

Accumulation

Rotational Crop

This study was conducted in a green house.

In this study radioactive thiodicarb was applied to Norfolk sandy loam at an equivalent rate of 5 lb AI/Acre. The treated soil was aged for 30 days in the green house and 3 plantings at day 30, 120 and 365 were made in succession.

The degradation products present in rotational crops include methomyl, methomyl oxime and methomyl methylol. ^{14}C residue level in lettuce planted 30 days after treatment was the highest (0.618 ppm). In corn and soybean, planted 120 days after treatment, the ^{14}C residues ranged between 0.003 to 0.08 ppm. The ^{14}C residue levels in soil were 4.28 and 0.48 at 30 and 395 days after treatment, respectively. Thiodicarb and methomyl were the only products identified in the treated soil.

Fish Accumulation Studies

Two separate studies, with ^{14}C-acetyl thiodicarb having two different exposure systems, a flow through system using bluegill sunfish and a static system using channel catfish have been submitted. These studies were conducted to determine the fish bioconcentration properties under the two systems. In both the studies, only radiometric analysis for residues in water, edible tissue, nonedible tissue, and whole fish during uptake of a 30 day period and during a 14 day depuration period, has been reported. The maximum bioconcentration factors of ^{14}C residues during uptake in whole fish were 13.7 for catfish and 5 for bluegill which indiate a low uptake rate in fish. Depuration of pesticide residues in both catfish and bluegill sunfish is relatively slow (t 1/2 $\leq$14 days), indicating possible persistence of residues in fish upon constant pesticide exposure. In these studies, at specific time intervals during the 30 day exposure, the characterization of metabolites was not shown.

However, in two additional studies, the analyses and characterization of metabolites are provided for bluegill sunfish and channel fish subjected to a single dose of 0.15 ppm and 0.073 of [14C]-acetyl thiodicarb respectively, during 4 day exposure.

Upon a single dose exposure study of 4 days (under static conditions) of [^{14}C] acetyl UC 51762, bluegill sunfish was found to contain 0.2% of thiodicarb, 20% of methomyl and 20% methomyl oxime. The radioactive residues were present to an extent of 80% in the non-edible tissue. About 50% of the total ^{14}C in fish has not been characterized.

A similar 4 day single dose exposure study of [14C] acetyl UC 5172 with channel fish in water was conducted in a static system. Methomyl oxime was the only compound identified in the fish tissues, accounting for 63% of total residues. About 37% of ^{14}C-residues in the fish (represented as water soluble, unextractable and volatile) have not been identified. The water sample in the residue system was found to contain about 96% methomyl and 0.9% methomyl oxmine.

103.0 Toxicological Properties

Test Species	Test	Results	Test material
Bobwhite	Acute Oral LD50	2023 mg/kg	Tech.
Bobwhite	Dietary LC50	5620 ppm	Tech.
Mallard	Dietary LC50	5620 ppm	Tech.
Rainbow	96-hr LC50	2.55 ppm	Tech.
Bluegill	96-hr LC50	1.21 ppm	Tech.
Daphnia	48-hr LC50	53 ppb	Tech.

Note: All the above tests were rated core.

Rat	Acute Oral LD50	160 mg/kg	Tech.
Rat	Acute Oral LD50	171 mg/kg	Tech.
Rat	Acute Oral LD50	180 mg/kg	Tech.
Mouse	Acute Oral LD50	226 mg/kg	Tech.
Guinea pig	Acute Oral LD50	160 mg/kg	Tech.

Test Species	Test	Results	Test material
Rainbow	Embryo-larvae	No dose related effects at a concentration of 1 ppm. MATC assumed to be between 1 ppm and 1.06 ppm.	Tech.
Daphnia	Life cycle	MATC is between 9 and 18 ppb. The 48 hr-LC50 is around 50 ppb.	Tech.

Note: The latter two test were rated core.

104.0 Hazard Assessment

104.1 Discussion

In previous reviews concern was raised over potential impacts to aquatic environments from the use of thiodicarb. This concern was due to its extreme toxicity to aquatic invertebrates, LC50= 53 ppb, half-life of approximately 80 days in water,* and estimates that thiodicarb at proposed use rates could reach aquatic habitats at concentrations greater than 30 ppb. Due to this, further tests were suggested to better define these potential problems. The Rainbow Trout Embryo-larvae test which was suggested, showed the MATC to be between 1 and 1.06 ppm, well above predicted environmental concentrations. However, the Daphnia Life Cycle Test showed a MATC of between 9 and 18 ppb, within the range of concern .

In conversations with Robert Holst of EFB, it was learned that since the above calculations were made by EFB on Thiodicarb, they have refined their model used to predict EEC's and, therefore, a re-evaluation was warrented.

The new estimate showed a maximum of 5.41 ppb thiodicarb dissolved in the aquatic environment (see attached report). This new estimate along with the additional tests indicate that thiodicarb should not reach aquatic habitat in significant concentration to result in adverse effects. Considering these estimates for thiodicarb, it appears that the probability that its major degradate, methomyl, would not reach aquatic habitat in significant levels to cause adverse effects. (LD50 of methomyl to Daphnia is equal to 31 ppb).

As pointed out in previous reviews, expected residues of thiodicarb in and around fields is well below levels found toxic to avian or mammalian species.

104.1.1 Likelihood of Exposure of Nontarget Organisms.

While the proposed label amendment would significantly increase exposure, as discussed above, expected environmental concentrations are below levels which would indicate potential adverse effects.

104.1.2 Endangered Species Consideration

The proposed label amendment should not adversely influence endangered species.

104.1.3 Adequacy of Toxicity Data.

All registration requirements for the proposed label amendment for evaluating hazard to non-target species appear to be satisfied.

107.0 Conclusion

EEB has completed an incremental risk assessment of the proposed registration of Thiodicarb for use on field and sweet corn. Based upon the available data EEB concludes that the proposed uses provide for a significant increase in exposure, but not in risks to non-targets.

Labeling

If the current label does not have statements reflecting the following, they should be added to the amended label:

This pesticide is extremely toxic to aquatic organisms. Do not apply it directly to water or wet lands. Do not contaminate water by the cleaning of equipment or disposal of wastes. Do not apply when conditions favor drift from the target area. HTC

This pesticide is toxic to aquatic invertebrates. Do not apply directly to water or wet lands. Runoff from treated areas may be hazardous to aquatic organisms in adjacent aquatic sites. Do not contaminate water by cleaning of equipment or disposal of wastes.

Ed Fite
Wildlife Biologist
Ecological Effects Branch
Ed Fite 1/28/83

Norm Cook
Section Head
Ecological Effects Branch
Norman Cook 1-28-83

for H. T. Craven
Clayton Bushong, Chief
Ecological Effects Branch
1-28-83

11

System: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
Chemical: THIODICARB
Inputs: .000001 kg, day 0; .010 kg, day 5; .100 kg, day 10

```
5.413E-03 I          B
          I           BB
          I             BB              B = Water Column Ave.
          I               BB                Dissolved (mg/l)
          I                 BBB         C = Benthic Ave. Dissolved
3.609E-03 I                    BBB          (mg/l)
          I                       BB
          I                         BBBB
          I                             BBBB
          I                                 BBBB
1.804E-03 I                                     BBBBB
          I                                          BBBBBBB
          I                                                 BB
          I                       CCCCCCCCCCCCCCCCCCCCCCCCCCCC
          I     BBBBBB  CCCCCCCCCC
0.000     ICCCCCCCCCCCCC
           +----+----+----+----+----+----+----+----+----+----+
           0    5   10   15   20   25   30   35   40   45   50
                              Time, Days
```

System: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
Chemical: THIODICARB
Inputs: .000001 kg, day 0; .010 kg, day 5; .100 kg, day 10

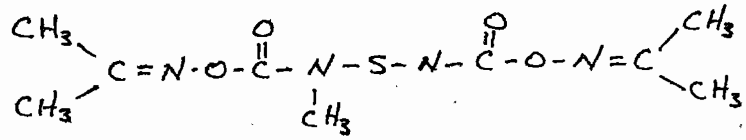
```
9.987E-03 I          B            B = Water Column Ave.
          I           BB              Sorbed (mg/kg)
          I             BB        C = Benthic Ave.
          I               BB          Sorbed (mg/kg)
          I                 BBB
6.658E-03 I                    BBB
          I                       BB
          I                         BBBB
          I                             BBBB
          I                                 BBBB
3.329E-03 I                                     BBBBB
          I                                          BBBBBBB
          I                                                 BB
          I                       CCCCCCCCCCCCCCCCCCCCCCCCCCCC
          I     BBBBBB  CCCCCCCCCC
0.000     ICCCCCCCCCCCCC
           +----+----+----+----+----+----+----+----+----+----+
           0    5   10   15   20   25   30   35   40   45   50
                              Time, Days
```

Shaugh. No. 114501

Common Name: Thiodicarb

Chemical Name: N,N[1][thiobis[(methylimino)carbonloxy]]bis-dimethyl ester

Structure:



Chemical Properties:

Molecular Weight: 354.5

Solubility (ppm): 35 (25 °C)

Partitioning:

Clay Loam 1.34
Loamy Sand .58
Sandy Loam 1.22

K_{ow} 45 K_{oc} ______ K_d=K_{abs}=K_{ps} ______

Hydrolysis (halflife hrs.)

(pH 3) 206 hr (pH 7) long term study (>150 days) hr (pH 9) 22 hr

K_{ah} 3.36×10^{-3} K_{nh} 2×10^{-4}/hr K_{bh} 3.16×10^{-2}/hr

Photolysis (halflife hrs.)

1944 hrs K_{dp} 8.6×10^{-3}/day (3.5×10^{-4}/hr)

Degradation (halflife hrs.)

Soil (Aerobic)(pH 6-8) 72-120 hr K 9.6×10^{-3} to 5.7×10^{-3}/hr

Soil (Anaerobic)(pH) ______ hr K ______

Water (Type Pond Sterile pH) 144-400 hr K 4.6×10^{-3} to 1.7×10^{-3}/hr

Bacteriological

Soil (Type ______) ______ hr K ______

Water (Type ______) ______ hr K ______

Vapor Pressure: 4.3×10^{-5} mmHg at 25°C

Evaporation: ______

(Information taken from company data in EFB review of 1 May 1981)

13

Fites request to EAB for an EEC

6.5

19 JAN 1983

MEMORANDUM

TO: Dr. Robert Holst
Environmental Fate Branch
Hazard Evaluation Division

THRU: Norm Cook, Head, Section #2
Ecological Effects Branch
Hazard Evaluation Division

THRU: Clayton Bushong, Chief
Ecological Effects Branch
Hazard Evaluation Division

SUBJECT: Request for Estimated Environmental Concentration for Thiodicarb.

As per our conversation, EEB requires an Estimated Environmental Concentration from the Environmental Fate Branch for Thiodicarb for its proposed use on Field and Sweet Corn. Specifically, as we discussed, we need EEC's for the parent compound and major degradates for Lentic and Lotic Situations. Your cooperation is greatly appreciated.

Ed Fite
Ecological Effects Branch
Hazard Evaluation Division TS-769

cc. L. Touart

TS-769:EFite:dmf:Rm 1128A:CM-2:557-9307:1/19/83