

Shaughnessy No.: 090301

Date Out of EAB: _____

To: Mr. Edward Allen
Product Manager #12
Registration Division (TS-767)

From: Emil Regelman, Supervisory Chemist
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached, please find the EAB review of...

Reg./File # : 352-361

Chemical Name: Methomyl

Type Product : Insecticide

Product Name : Lannate

Company Name : E.I. du Pont de Nemours and Company, Inc.

Purpose : Addendum to a Standard. Review of Photolysis study on soil.

Action Code(s): 606

EAB #(s) : 70018

Date Received: 10/6/86

TAIS Code: _____

Date Completed: _____

Total EAB Review Time: 2 days

Monitoring submitted: _____

Monitoring requested: _____

Deferrals to: _____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch _____

1. CHEMICAL: Common name:

Methomyl

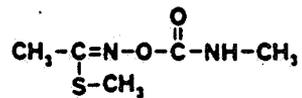
Chemical name:

S-Methyl-N-[(methylcarbamoyl)oxy]thioacetimidate

Trade name(s):

Lannate, Lanox 90, Lanox 216, Mu-Rait II, Nudrin,
SD 14999

Structure:



Formulations:

90% WP, a liquid containing 1.8 lb ai/gallon, a liquid containing 2.4 lb ai/gallon for L.V. applications

Physical/Chemical properties:

Molecular formula: C₅H₁₀N₂O₂S.

Molecular weight: 162.2

Physical state: White crystalline solid.

Melting point: 78-79°C.

Solubility: Water, 5.8 g/100 g.
Methanol, 100 g/100 g.

2. TEST MATERIAL:

Active ingredient, [1-¹⁴C] methomyl.

3. STUDY/ACTION TYPE:

Review photolysis study on soil to support continued registration of methomyl.

4. STUDY IDENTIFICATION:

The following study was reviewed as a new submittal:

Swanson, M.B. 1986. Photodegradation of [1-¹⁴C] methomyl on soil. Document No. AMR-611-86. Prepared and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. Acces. No. 265281.

5. REVIEWED BY:

Padma R. Datta, Ph.D.
Chemist
Review Section #3
EAR/HED

Signature: _____

Date: _____

6. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review Section #3
EAR/HED

Signature: _____

Date: _____

7. CONCLUSIONS:

The submitted study, "Photodegradation of [1-¹⁴C] Methomyl on Soil", was conducted in accordance with the Pesticide Assessment Guidelines (Subdivision N) and 40 CFR §158.130. This study is scientifically valid and acceptable to EAB. The results of this study fulfill the data requirement of photodegradation on soil (§161-3) of the Methomyl Registration Standard and support the continued registration of methomyl.

8. RECOMMENDATION:

EAB recommends the Registration Division (RD) inform the DuPont Company that the submitted study, "Photodegradation of [1-¹⁴C] Methomyl on Soil" (DuPont Document No. AMP-611-86), is acceptable to EAB. This study fulfills the data requirement on photodegradation on soil (§161-3) of the Methomyl Registration Standard and supports the continued registration of methomyl.

9. BACKGROUND:

In a letter dated May 26, 1982, DuPont Company responded to the Data "Call-In" (DCI) Notice under Section 3(c)(2)(B) of FIFRA, as amended, 1972. (For details, see DuPont Company's letter of response to methomyl continued registration). In this letter DuPont Company requested: (1) a discussion meeting for all data requirements under the DCI Notice; and, (2) a waiver for the photodegradation study of methomyl, citing three previously submitted studies reflecting photolysis of methomyl on soil and in water.

On October 13, 1982, Mr. Hudson Boyd, Chemist, Review Section #3 of EFB (now EAR), was assigned the DuPont letter for review. He completed his review on the due date, December 6, 1982. Mr. Boyd pointed out that DuPont Company researchers used questionable scientific methodologies to conduct the three previously submitted photolysis studies under natural

9. BACKGROUND (CONTD'):

sunlight, and recommended against the requested waiver. However, EAB agreed to the photodegradation study waiver request over Mr. Boyd's objection. This review was sent to RD on December 8, 1982, after approval from Emil Regelman, Acting Chief of Review Section I. (For details, refer to EFB review #9, December 8, 1982.)

Despite this granting of the requested data waiver, the DuPont Company submitted a photodegradation study on October 6, 1986 entitled, "Photodegradation of [1-¹⁴C] Methomyl on Soil" (DuPont Document No. AMR-611-86). Dynamac reviewed this study and found it scientifically valid and acceptable to support the data requirement "Photodegradation on Soil" (§161-3) of Subdivision N of the Pesticide Assessment Guidelines and 40 CFR §158.130.

EAB concurs with Dynamac's finding on the validity and acceptability of this study. The results fulfill the photodegradation on soil (§161-3) data requirement of the Methomyl Registration Standard and the continued registration of methomyl.

This study did not contain information on the specific activity of the radiolabeled methomyl which was used. My telecon on March 19, 1987, with Mr. J. Anderson of the DuPont Company revealed that the radiolabeled [1-¹⁴C] Methomyl used in this study had a specific activity of 19.3 µCi/mg (4.28 x 10⁴ dpm/µg) and a purity of 98%. This information has now been incorporated into the DER of this study prepared by Dynamac.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See attached review of individual study.

11. COMPLETION OF ONE-LINER:

N/A.

12. CBI APPENDIX:

All data reviewed here are considered CBI by the registrant and must be treated as such.

METHOMYL

Final Report

**Task 1: Review and Evaluation of
Individual Studies**

Contract No. 68-02-4250

APRIL 15, 1987

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

METHOMYL

Table of Contents

	<u>Page</u>
Scientific Study	
1. Photodegradation on soil.	1
Appendix	7

CASE GS -- METHOMYL STUDY 1 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT
-----FICHE/MASTER ID No MPID CONTENT CAT 01
Swanson, M.B. 1986. Photodegradation of [1-¹⁴C]methomyl on soil. Document
No. AMR-611-86. Prepared and submitted by E.I. du Pont de Nemours and
Company, Inc., Wilmington, DE. Acc. No. 00265281.
-----SUBST. CLASS = S.
-----DIRECT RVW TIME = 4 (MH) START-DATE END DATE
-----REVIEWED BY: W. Higgins
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500
-----APPROVED BY: P. Datta
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-9733

SIGNATURE:

DATE:

CONCLUSIONS:Degradation - Photodegradation on Soil

1. This study is scientifically valid.
2. [1-¹⁴C]Methomyl (radiochemical purity 98%), at ~1 lb ai/A, degraded with a half-life of 34 days (registrant-calculated) on silty clay loam soil irradiated with natural sunlight at 24-28°C. After 30 days of irradiation, 53% of the applied methomyl remained undegraded. All extractable radioactivity was identified as [1-¹⁴C]methomyl using HPLC and TLC. [1-¹⁴C]Acetonitrile, which was the only volatile compound, totaled 40% of the applied radioactivity in irradiated samples at 30 days posttreatment. In the dark controls, [1-¹⁴C]methomyl was stable for the duration of the study.
3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of methomyl on soil irradiated with natural sunlight.

MATERIALS AND METHODS:

A slurry of air-dried Keyport silty clay loam soil (50% sand, 67.5% silt, 28.0% clay, 1.4% organic matter, pH 6.8, CEC 6.25 meq/100 g) and water was spread on glass microscope slides to a thickness of 1-mm using a TLC spreader and allowed to air dry for several days. [1-¹⁴C]Methomyl (radiochemical purity 98%, specific activity 19.3 μ Ci/mg, 4.28×10^4 dpm/mg, New England Nuclear) dissolved in N,N-dimethylformamide was applied evenly by syringe to the soil layer at 161 μ g/slide (~1 lb ai/A). The soil slides were placed on two stainless steel heat exchangers, each of which was contained inside a water-tight Lucite box (Figure 1). The temperature of the slides was controlled by pumping 25°C water through the heat exchanger at a flow rate of 1 L/minute using a refrigerated circulating water bath. The top of each photolysis apparatus had a quartz window through which samples were irradiated. The photolysis apparatus containing the dark control samples was covered with aluminum foil to exclude light. Each photolysis apparatus was equipped with vents which allowed a 10 mL/minute stream of air to be drawn through a gas washing bottle containing anhydrous calcium sulfate, through the apparatus itself, and then through two charcoal tubes, one containing 2-ethoxyethanol, and one bottle containing 1.0 M sodium hydroxide. Both photolysis apparatus were placed on a platform on the roof of a building at the E.I. du Pont de Nemours Co., Inc., Experimental Station in Wilmington, DE (39°40'N latitude) from July 31 to August 30, 1986. Soil temperature was maintained between 24-28°C. A pyranometer was used to continuously monitor the solar radiation striking the soil samples (Table 1). Irradiated soil slides were removed from the photolysis apparatus at 2, 5, 8, 15, and 30 days posttreatment. Soil slides were removed from the dark control apparatus at 8, 15, 22, and 30 days posttreatment. At each sampling interval, all gas trap solutions were removed for analysis and replaced with fresh solutions. If soil samples could not be analyzed on the day they were taken, the soil was wrapped in aluminum foil and placed in a freezer at -20°C until analysis. Charcoal tubes were replaced every day.

Each soil sample was scraped off of the slide and extracted three times by shaking for 20 minutes with methanol. Each extraction mixture was centrifuged, the supernatant was decanted, and all three extracts were combined. The radioactivity of the combined extract was determined by LSC. Degradates were identified by HPLC and TLC using silica gel plates developed in ethyl acetate. Plates were visualized using autoradiography and quantitated using a linear analyzer. Radioactive compounds were identified by cochromatography with standards, which were visualized with UV light. Volatiles collected in the charcoal tubes were extracted by mixing the charcoal with N,N-dimethylformamide and agitating the mixture overnight. The mixture was centrifuged and aliquots of the supernatant were fractionated by HPLC. The compounds in the fractions were identified according to retention time and were quantified by LSC.

REPORTED RESULTS:

[1-¹⁴C]Methomyl degraded with a registrant-calculated half-life of 34 days when irradiated by natural sunlight. After 30 days of irradiation, 53% of the applied methomyl remained undegraded (Table 2). All extractable

radioactivity was identified as [1-¹⁴C]methomyl. [¹⁴C]Acetonitrile, which was the only volatile compound, totaled 40% of the applied radioactivity in irradiated samples at 30 days posttreatment.

[1-¹⁴C]Methomyl in the dark controls ranged from 96% of the applied at day 0 to 99% at day 30. [¹⁴C]Acetonitrile (volatile) totaled 4% of the applied radioactivity at day 30.

DISCUSSION:

1. The registrant called the test soil a silt loam, but it was a silty clay loam according to the USDA Soil Textural Classification System and was referred to as such. ←
2. Raw data were not provided.

10

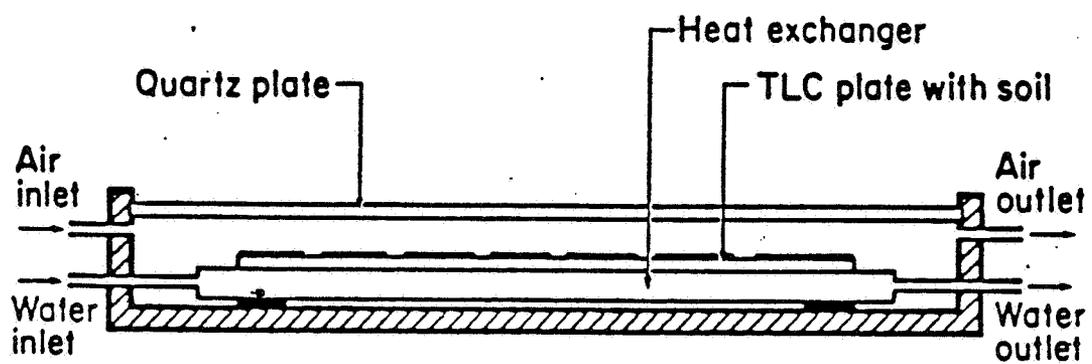


Figure 1. Photolysis apparatus.

Table 1. Solar radiation (Watt-hours/m²) measured by pyranometer at the E.I. du Pont de Nemours Co., Inc., Experimental Station in Wilmington, DE (39°40'N latitude; July 31, 1986-August 30, 1986).

Sampling interval (days)	Total energy per day	Cumulative energy	Cumulative energy at sampling ^a
0	1708	1708	
1	4933	6641	
2	4020	10661	10293
3	3596	14257	
4	7298	21555	
5	5908	27463	26135
6	5665	33128	
7	3448	36576	
8	3979	40555	39757
9	6560	47115	
10	5792	52907	
11	4917	57824	
12	4486	62310	
13	6075	68385	
14	6499	74884	
15	6404	81288	79457
16	3878	85166	
17	3257	88423	
18	5301	93724	
19	3511	97235	
20	3161	100396	
21	897	101293	
22	6361	107654	106038
23	5861	113515	
24	6911	120426	
25	6547	126973	
26	6092	133065	
27	3654	136719	
28	3185	139904	
29	6986	146890	
30	5064	151954	151954

^a Cumulative energy up to time of sampling (~3:00 p.m.).

Table 2. Distribution of radioactivity (% of the applied) in silty clay loam soil treated with [¹⁴C]methomyl (radiochemical purity 95%) at ~1 lb ai/A and irradiated with natural sunlight.

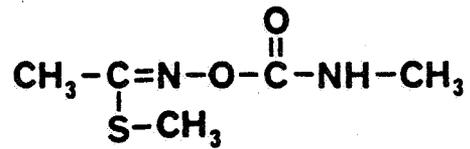
Sampling interval (days)	Methomyl ^a	Unextractable	Acetonitrile (volatile) ^b	Total
<u>Irradiated</u>				
0	96	--	--	--
2 ^c	91	3	12	106
5	84	2	15	101
8	80	3	20	103
15	64	3	38	105
22	54	4	39	97
30 ^c	53	4	40	97
<u>Dark controls</u>				
0	96	2	0	98
8	103	3	2	108
15	100	2	3	105
22	99	4	4	107
30 ^c	99	4	4	107

^a Methomyl accounted for 100% of the extractable radioactivity.

^b Acetonitrile accounted for 100% of the volatile radioactivity.

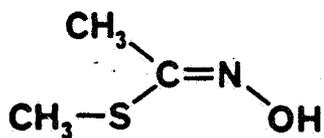
^c Values represent the average of duplicate samples.

APPENDIX
METHOMYL AND ITS DEGRADATES

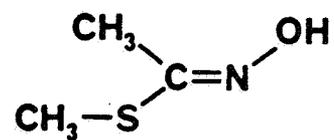


S-Methyl N-[(methyl (carbamoyl)oxy]thioacetimidate

(Methonyl)



S-Methyl N-hydroxythioacetimidate
(SYN isomer)



S-Methyl N-hydroxythioacetimidate
(ANTI isomer)