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To: Barbara Briscoe, Product Manager #51  
 Special Review and Reregistration Division (H7508W)

From: Emil Regelman, Supervisory Chemist  
 Environmental Chemistry Review Section #2  
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief  
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

Reg./File # :068102-064715, 068102-001448, 068102-033677

Chemical Name :Methylene-bis(thiocyanate)

Type Product :MICROBIOCIDES/MICROBIOSTAT

Product Name :VEDEXIL

Company Name :Methylene-bis(thiocyanate) Task Force

Purpose :Review of data package submitted to satisfy environmental fate data requirements. Review of change in status request for Terrestrial Field Dissipation and Aquatic Field Dissipation data requirements and waiver request for Spray Drift data requirements.

Action Code :165, 627, 614, 614

EFGWB #(s): 91-0488, 91-0687, 92-0130, 92-0129

Total Review Time: 7 days

**EFGWB Guideline/MRID Summary Table: The review in this package contains...**

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1. CHEMICAL:

Common name:

Vedexil

Chemical name:

Methylene-bis(thiocyanate)

Chemical Abstract Registry #:

6317-18-6

Structure:



Formulation:

Manufacturing-use product (99 % pure)

Active Ingredient: Methylene-bis(thiocyanate) 98 %

Physical/Chemical properties:

Molecular formula:  $\text{C}_3\text{H}_2\text{S}_2\text{N}_2$

Molecular weight: 130

Physical state: Crystalline solid

Color: White

Melting point: 105-107 °C

Density: 2.0 g/ml

Stability: Stable to 100 °C

Reactivity: Decomposes in alkaline solution

Vapor Pressure:  $1.22 \times 10^{-4}$  Torr

Solubility in water:  $2.8 \times 10^5$  ppm

Solubility (% w/w at 25 °C):

acetone: 29  
acetonitrile: 30  
dimethylformamide: 44  
dioxane: 24  
ethylene glycol: 4  
monoethyl ester: 17  
methyl ethyl ketone: 20

2. TEST MATERIAL:

Study 1: Methylene-bis(thiocyanate) (commercial grade)

Study 2 & 3: Methyl-labeled [ $^{14}\text{C}$ ]methylene-bis(thiocyanate) (radiochemical purity >98 %)

3. STUDY ACTION TYPE:

Review of Hydrolysis, Photodegradation in water and Leaching/adsorption/desorption studies submitted to satisfy the Environmental Fate data requirements for registration of Methylene-bis(thiocyanate).

Review of change in status request for Terrestrial Field Dissipation and Aquatic Field Dissipation data requirements and a waiver request for Spray Drift data requirements 201-1 and 202-1.

4. STUDY IDENTIFICATION:

Macdonald, I.A. and D.A. Howes. 1985. The determination of the hydrolysis of methylene-bis(thiocyanate) as a function of PH. HRC Project No. A & W 460/85626. Unpublished study performed by Huntington Research Centre Ltd., Cambridgeshire, England, and submitted by Buckman Laboratories, Memphis, TN. (00150229)

Cameron, B.D., B.E. Hall, and M. Phillips. 1991. Artificial sunlight photodegradation of [<sup>14</sup>C]MTC in buffered aqueous solution. IRI Project No. 380228. Unpublished study performed by Inveresk Research International, Tranent, Scotland, and submitted by Buckman Laboratories, Memphis, TN. (41897101)

Cameron, B.D., B.E. Hall, and R. Jackson. 1990. The adsorption and desorption characteristics of [<sup>14</sup>C]MTC in soil. IRI Project No. 380212. Report No. 7439. Unpublished study performed by Inveresk Research International, Tranent, Scotland, and submitted by Buckman Laboratories, Memphis, TN. (41764601)

5. REVIEWED BY:

Mah Shamim, Ph.D.  
Chemist  
EFGWB/EFED/OPP  
Review Section #2

Signature: M. Shamim

Date: 1/2/92

6. APPROVED BY:

Emil Regelman  
Supervisory Chemist  
EFGWB/EFED/OPP  
Review Section #2

Signature: E. Regelman

Date: JAN 7 1992

7. CONCLUSION:

The Registrant, Methylene-bis(thiocyanate) Task Force, has submitted a number of studies outlined in the study identification section to support the registration of Methylene-bis(thiocyanate) for use on Aquatic nonfood industrial, Terrestrial nonfood, Indoor food/nonfood, and Residential indoor/outdoor sites.

161-1 HYDROLYSIS: (MRID #00150229)

The study on Hydrolysis was reviewed earlier (1/23/86) and was found to be acceptable. However, this study has been rereviewed (see DER) and was found unacceptable to fulfill the EFGWB data requirements due to the following deficiencies:

- \* The material balances were incomplete for PH 7 and 9 test solutions. Only 17.5 % of the starting material was identified as the parent at 144 hours after incubation in PH 7 buffer solution. All of the starting material hydrolysed and was unaccounted for at 17 hours post-treatment in PH 9 test solution;
- \* The degradates, aldehyde and thiocyanate, were analyzed for only one sampling interval (23 hours posttreatment) for PH 7 test solution and two sampling intervals (265 & 445 minutes posttreatment) for PH 9 test solutions;
- \* The test substance was not technical grade for PH 5, 7, & 9 test solutions.

Because of the above deficiencies, submission of additional data cannot repair this study. A new study is required. When conducting a new study, the registrant must use (as a minimum) a technical grade of the active ingredient, assure complete material balance and analyze for all degradates (eg., formaldehyde, thiocyanate ion etc.) at all sampling intervals.

The Registrant reported no significant degradation of unlabeled commercial grade methylene-bis(thiocyanate) when it was incubated in the dark in a PH 5 buffer solution at a nominal test concentration of 250  $\mu\text{g/ml}$  for 30 days at 25 °C. However, under similar incubation conditions, methylene-bis(thiocyanate) hydrolyzed in PH 7 & 9 buffer solutions with the registrant calculated half-lives of 21.2 hours and 133.5 minutes respectively. Two degradates, formaldehyde and thiocyanate ion were identified in both PH 7 and 9 test solutions.

161-2 PHOTODEGRADATION IN WATER: (MRID #41897101)

This study is scientifically sound but does not meet subdivision N guidelines due to the following reasons:

- \* No attempt was made to identify the two degradates present at a maximum concentration of 12.8 and 20.2 % of the extracted radioactivity.

In order for this study to satisfy photodegradation in water data requirement, the Registrant must isolate the photodegradates using chromatographic methods such as HPLC or GC and confirm their identities by Mass Spectrometry (MS) and/or infra Red Spectroscopy (IR).

Methyl-labeled [<sup>14</sup>C]methylene-bis(thiocyanate) (radiochemical purity ≥ 98 %), at a nominal concentration of 240 ppm, photodegraded slowly in sterile aqueous buffer solution (PH 5) that was irradiated with an artificial light source (xenon light) at 23.8-26.0 °C for 372 hours. At the end of the irradiation period, parent methylene-bis(thiocyanate) comprised of 68.2-73.8 % of the total radioactivity compared to 92-99 % of the total radioactivity in the dark controls. Two degradates present at maximum concentrations of 7.3-12.9 and 16.9-20.2 % of the extracted radioactivity remained uncharacterized.

163-1 LEACHING/ADSORPTION/DESORPTION: (MRID #41764601)

This study is scientifically sound but is not acceptable to fulfill mobility data requirements for unaged methylene-bis(thiocyanate) in soil due to the following deficiencies:

- \* Adsorption of methylene-bis(thiocyanate) to the soil was determined by LSC analysis of the supernatant after equilibrium had been reached. The soils were not analyzed to confirm adsorption and to assure complete material balance.
- \* Adequate methodology was not used to confirm the presence of methylene-bis(thiocyanate) or its degradates in the supernatants after adsorption and desorption. Identification of methylene-bis(thiocyanate) in the supernatants was based on the assumption that any radioactivity present in the supernatants was the undegraded and non-modified starting material. A complete characterization of the chemical components in the supernatants was not carried out.

Since the soils were not analyzed to confirm adsorption and the supernatants were not analyzed to confirm the presence of parent methylene-bis(thiocyanate) or its degradates, the problems with this study cannot be resolved by submission of additional data. A new study is required. When conducting a new study, the Registrant must analyze the soils after equilibrium to confirm adsorption and to complete material balance. Also, the registrant must analyze the supernatants, after adsorption and desorption, by other analytical techniques (such as HPLC and GC) to identify not only the parent methylene-bis(thiocyanate) but to characterize any degradate that may be present. Additional data is needed on the mobility of aged methylene-bis(thiocyanate) residues in soil.

Methylene-bis(thiocyanate) appears to be very mobile in sand, sandy loam, silt loam and silty clay loam soils with Freundlich  $K_{ads}$  values of 0.4447, 0.3934, 0.4836, and 0.8140 respectively. The  $K_{des}$  values are 2.737 for the silty clay soil, 3.274 for the silt loam soil, 3.422 for the sand soil, and 2.913 for the sandy loam soil.

## ENVIRONMENTAL FATE ASSESSMENT

Since the environmental fate data base is incomplete at this time, a complete environmental fate assessment cannot be made. Based on the supplemental data derived from the three unacceptable studies, it appears that methylene-bis(thiocyanate) is stable to hydrolysis at PH 5 and is the only compound identified at all sampling intervals. However, under basic conditions methylene-bis(thiocyanate) readily hydrolyses ( half-lives of 21.2 hours and 133.5 minutes respectively) to form at least two degradates, formaldehyde and thiocyanate ions.

It photodegrades relatively slowly with parent methylene-bis(thiocyanate) comprising of 73.8 % of starting material at the end of 372 hours of irradiation period. Two photodegradates present in the irradiated samples remained unidentified.

Methylene-bis(thiocyanate) appears to be highly mobile in sand, sandy loam, silt loam, and silty clay loam soils with respective Freundlich  $K_{ads}$  values of 0.4447, 0.3934, 0.4836, and 0.8140. It is also readily desorbed with  $K_{des}$  values of 2,737 for silty clay soil, 3.274 for the silt loam soil, 3.422 for the sand soil, and 2.913 for the sandy loam soil.

Since methylene-bis(thiocyanate) has aquatic uses and under alkaline conditions is known to form thiocyanate ions, EFGWB has concerns about the mobility of thiocyanate salts in soils and their potential to leach to ground water. These concerns are heightened by the fact that both methylene-bis(thiocyanate) and its degradates are highly toxic to humans, fish and wildlife. Both methylene-bis(thiocyanate) and thiocyanate salts, under strong acidic conditions release toxic gases such as thiocyanic acid,  $H_2S$ ,  $CS_2$ , as well as  $CO$ ,  $NO_x$  and  $SO_2$ . Whether methylene-bis(thiocyanate) has potential to reach the ground water will depend on a number of factors such as persistence of this chemical in soil, the type and amount of degradates that are formed and their mobility in soil. A more comprehensive assessment will be made when additional data on the mobility of aged methylene-bis(thiocyanate) residues in soil, aerobic soil metabolism, and soil field dissipation have been received and evaluated.

### 8. RECOMMENDATIONS:

The Registrant should be informed of the following:

- a. The study on Hydrolysis, reviewed and previously accepted (1/23/86) was rereviewed and found unacceptable because of the deficiencies noted in the conclusion section. A new study must be submitted. In the new study, the Registrant must address the problems noted in the conclusion section and in the data evaluation section.
- b. The study on Photodegradation in water is scientifically sound but does not satisfy the environmental fate data requirements because of the deficiencies noted in the conclusion section. This study will satisfy the Photodegradation in water data requirement by submission of additional data as requested in the conclusion section and in the data evaluation section.

- c. The study on Leaching/adsorption/desorption is unacceptable due to the deficiencies noted in the conclusion section. A new study is required that should take into account the deficiencies noted in the conclusion and data evaluation section.
- d. The Registrant has requested a change in status, from required to reserved, for Terrestrial Field Dissipation and Aquatic (sediment) Field Dissipation data requirements pending the completion of on-going environmental fate studies (Photodegradation in soil, Aerobic and Anaerobic soil metabolism). EFGWB cannot concur with this request because these data are required to determine fate of methylene-bis(thiocyanate) in soil and its leaching potential in ground water especially when the supplemental data from Leaching/adsorption/desorption has determined this chemical to be highly mobile in a number of soils. However, the Registrant should not initiate these studies until Photodegradation in soil, Aerobic soil metabolism and Anaerobic soil metabolism studies have been completed and the resulting metabolites have been identified. The Registrant should request suitable time extensions to complete these studies.
- e. The Registrant has also requested waivers for Droplet Size Spectrum (201-1) and Drift Field Evaluation (202-1) data requirements. The waiver requests are inappropriate because these data are not required for the proposed use pattern. The trigger for these data requirements are application methods which include aerial spraying or use of air carrier mist blowers. Since methylene-bis(thiocyanate) is applied by ground equipment only and its application does not include any of the above mentioned methods these data requirements are not triggered. Acute toxicity that was used as a trigger to initiate these data requirements is no longer valid since according to EEB non-target toxicity is not a criteria for Spray Drift studies and therefore these data requirements cannot be imposed. However, spray drift data may be required in the future if the Registrant decides to add aerial applications to the label.
- d. The status of the Environmental Fate data requirements for the registration of methylene-bis(thiocyanate) for the Terrestrial Nonfood, Aquatic Nonfood Industrial, Indoor/outdoor Residential, Indoor Food/Nonfood use pattern is as follows:

**Data Requirements For Methylene-bis(thiocyanate)**

Data Requirements	Use Pattern <sup>1</sup>	Does EPA have data to satisfy this requirement? (Bibliographic citation)		Additional data required by EPA
161-1 Hydrolysis	CFK	No		Yes <sup>2</sup>
161-2 Photodegradation in Water	CF	Partial		Yes <sup>3</sup>
162-1 Aerobic Soil Metabolism	CK	No		Yes
162-3 Anaerobic Aquatic Metabolism	F	No		Yes
162-4 Aerobic Aquatic Metabolism	F	No		Yes
163-1 Leaching/Adsorp/Desorp	CFK	No		Yes <sup>4</sup>
164-1 Terrestrial Field Dissipation (Soil)	CK	No		Yes
164-2 Aquatic Field Dissipation (Sediment)	F	No		Yes
165-4 Bioaccumulation in Fish	CF	No		Waived <sup>5</sup>

**OTHER DATA:**

Ground and/or Surface Water Monitoring	No	Reserved <sup>6</sup>
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**FOOTNOTES:**

- 1) The use patterns are coded as follows: Terrestrial Nonfood = C; Aquatic Nonfood Industrial = F; Outdoor Residential = K
- 2) The study on Hydrolysis (MRID #00150229), reviewed previously and accepted (1/23/86), was rereviewed and was found unacceptable due to the deficiencies noted in the conclusion and data evaluation sections. A new study must be submitted.
- 3) The study on Photodegradation in water (MRID #41897101) was found unacceptable due to lack of data on the photodegradates. In order for this study to satisfy the environmental fate data requirements, additional data on photodegradates in water must be submitted. However, if the Registrant is unable to repair this study, a new study must be submitted.
- 4) The study on Leaching/adsorption/desorption (MRID #41764601) was found unacceptable due to the deficiencies noted in the conclusion and data evaluation sections. A new study must be submitted. Additional data on the mobility of aged methylene-bis(thiocyanate) residues in soil is required.
- 5) This data requirement was waived in a previous DCI issued on March 7, 1991 and was based on low octanol/water coefficient ( $K_{ow} < 10$ ) and high water solubility ( $2.8 \times 10^2$  ppm) of the chemical indicating its lipophobic nature.
- 6) These data requirements are reserved pending results of laboratory and field dissipation studies.



9. BACKGROUND:

A. Introduction:

Methylene-bis(thiocyanate) is the active ingredient in a number of products used as microbiocides and preservatives. This chemical is supported by seven registrants who have formed a Methylene-bis(thiocyanate) Task Force to deal with its reregistration. The registrants who are part of the Task Force include:

- \* Akzo Chemicals
- \* Albright & Wilson Americas
- \* Ameribrom, Inc.
- \* Buckman Labs
- \* Calgon Corp.
- \* Vikings Industries
- \* Vineland Chemical

A data call-in was issued on March 7, 1991 that established the data requirements for the registration of methylene-bis(thiocyanate). The use patterns were identified by the LUIS Report dated 16 Feb., 1991. Products containing this active ingredient are used on a number of Aquatic Nonfood Industrial sites including water cooling systems, pulp and paper mill water cooling systems, industrial waste and disposal systems, industrial scrubbing systems, secondary oil recovery injection water and sewage systems. The Terrestrial Nonfood uses include wood pressure treatment to forest products. The Indoor Nonfood uses involve industrial adhesives, industrial coatings, resins/latex/polymer emulsions, oil storage tank bottom water additive, leather processing, metalworking cutting liquids, oil recovery drilling muds, latex paint cans, paper products, pasteurizer/warmer/cannery cooling water systems, industrial processing chemicals. Indoor Food use sites include food processing water systems. Indoor/Outdoor Residential use involves wood protection treatment to buildings, indoors as well as outdoors.

This pesticide is hazardous to humans and domestic animals. It is highly corrosive, causes severe skin irritation and eye damage. It may be fatal if swallowed or if contaminated food or water is ingested. It is highly toxic to fish and other aquatic animals. The label prohibits its use near water sources or discharge of effluent containing this chemical into lakes, streams, ponds, estuaries, oceans or public waters.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Refer to attached reviews.

11. COMPLETION OF ONE-LINER:

EFGWB one-liner was updated on 12/09/91

12. CBI APPENDIX:

Not applicable.

VEDEXIL

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DATA EVALUATION RECORD

STUDY 1

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CHEM 068102

Vedexil

§161-1  
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FORMULATION--00--ACTIVE INGREDIENT  
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STUDY ID 150229

Macdonald, I.A. and D.A. Howes. 1985. The determination of the hydrolysis of methylene bis thiocyanate as a function of pH. HRC Project No. A & W 460/85626. Unpublished study performed by Huntington Research Centre Ltd., Cambridgeshire, England, and submitted by Buckman Laboratories, Memphis, TN.  
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DIRECT REVIEW TIME = 6  
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REVIEWED BY: J. Harlin

TITLE: Staff Scientist

EDITED BY: L. Mickley  
W. Martin

TITLE: Staff Scientist  
Staff Scientist

APPROVED BY: W. Spangler

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TEL: 703-305-5025

SIGNATURE: 

CONCLUSIONS:

Degradation - Hydrolysis

1. This study is unacceptable and cannot be used to fulfill data requirements.
2. The rate of vedexil hydrolysis in sterile aqueous buffered solutions increased with increasing alkalinity. Vedexil did not hydrolyze in pH 5 solution, and hydrolyzed with half-lives of 21.2 hours and 133.5 minutes in pH 7 and 9 solutions, respectively. The degradates formaldehyde and the thiocyanate ion were identified in the pH 7 and 9 solutions.

3. This study has been reviewed earlier and was found acceptable. However, the study is rereviewed and is found unacceptable for the following reasons:

the material balances for PH 7 and 9 test solutions were incomplete;

the PH 7 and 9 test solutions were analyzed for the aldehyde and thiocyanate ions for only one and two sampling intervals respectively (23 hours posttreatment for PH 7; 265 mins and 445 mins posttreatment for PH 9). At all the remaining intervals the test solutions were analyzed for parent Vedexil only;

the test substance used for the entire study was of commercial grade.

4. Since the test substance was not technical grade or purer for the pH 5, 7, and 9 solutions, the material balances for the pH 7 and 9 solutions were incomplete, and the test solutions were analyzed for the degradates at only one or two sampling intervals, the problems with this study cannot be resolved with the submission of additional data. A new study must be submitted.

#### METHODOLOGY:

Vedexil ("commercial grade", test substance not further characterized, Tenneco Organics Limited) was finely ground and added at a nominal concentration of 250 ug/mL to duplicate Erlenmeyer flasks containing sterile (autoclaved) aqueous buffered solutions adjusted to pH 5 (0.1 M sodium hydroxide plus 0.1 M potassium hydrogen phthalate), pH 7 (0.1 M nitric acid plus 0.1 M tris buffer), and pH 9 (0.1 M sodium bicarbonate plus 0.1 M sodium carbonate). The test substance was dissolved in the buffer solutions using sonication, the flasks were sealed with sterilized glass stoppers, and the solutions were incubated at  $25 \pm 0.1$  C in the dark. Duplicate aliquots were removed for analysis at intervals up to 30 days for the pH 5 solution, up to 144 hours for the pH 7 solution, and up to 2460 minutes for the pH 9 solution.

Prior to analysis, aliquots of the pH 5 and 7 test solutions were diluted with glass-distilled water. The diluted aliquots of the pH 7 test solution and undiluted aliquots of the pH 9 test solution were acidified with 6 M nitric acid; the acidified aliquots of the pH 9 test solution were then diluted with glass-distilled water. Aliquots of the diluted solutions were analyzed for vedexil by HPLC using an Apex ODS column with a mobile phase of methanol:water (20:80) and UV detection (250 nm). Additional aliquots of the pH 7 (23 hours only) and pH 9 (265 and 445 minutes only) solutions were also analyzed for the degradates formaldehyde and thiocyanate ion. To analyze for formaldehyde, an aliquot of the test solution was added to a solution of phenylhydrazine hydrochloride. The resulting phenylhydrazine was

oxidized with aqueous potassium ferricyanide. The reaction solution was analyzed for formaldehyde using spectrophotometry (517 nm). To analyze for thiocyanate, aliquots of the test solutions were treated with 6 M nitric acid, 40% w/v aqueous ammonium ferric sulphate, and aqueous silver nitrate. The resulting mixture was titrated against 0.01 M ammonium thiocyanate to a "brownish/red" end point.

#### DATA SUMMARY:

Vedexil (purity unspecified), at a nominal concentration of 250 ug/mL, did not hydrolyze in a sterile buffered aqueous solution adjusted to pH 5 that was incubated in the dark at 25 C for 30 days (Table 7). Under similar incubation conditions, vedexil hydrolyzed at pH 7 and 9, with registrant-calculated half-lives of 21.2 hours and 133.5 minutes, respectively (Table 7). Two degradates,

formaldehyde and

thiocyanate ion,

were identified in both the pH 7 and 9 solutions.

In the pH 5 solution, the vedexil concentration was 252-258 ug/mL immediately posttreatment, and 246 ug/mL at 30 days posttreatment (Table 7).

In the pH 7 solution, the vedexil concentration was 257-262 ug/mL at 15 minutes posttreatment, 118 ug/mL at 23 hours, 65 ug/mL at 72 hours, and 45-46 ug/mL at 144 hours (Table 7). Formaldehyde was 1.31-1.38 ug/mL and thiocyanate ion was 81-82 ug/mL at 23 hours posttreatment (Tables 10 and 11).

In the pH 9 solution, the vedexil concentration was 263 ug/mL at 10 minutes posttreatment, 152 ug/mL at 78 minutes, 105-106 ug/mL at 145 minutes, 25 ug/mL at 445 minutes, and <1 ug/mL at 1020 minutes (Table 7). Formaldehyde was 0.97-0.99 ug/mL at 265 minutes and 2.37-3.06 ug/mL at 445 minutes (Table 10). Thiocyanate ion was 96-97 ug/mL at 265 minutes and 144 ug/mL at 445 minutes posttreatment (Table 11).

The material balance for the pH 5 solution was 98.4-103% of the initial concentration (reviewer calculated from Table 7). The material balances were incomplete for the pH 7 and 9 solutions.

#### COMMENTS:

1. The material balances for the pH 7 and 9 test solutions were incomplete. In the pH 7 test solution, only 17.5% of the starting material was accounted for (as vedexil) at 144 hours posttreatment.

In the pH 9 test solution, only 12% of the starting material was accounted for at 6.4 hours; all of the starting material was lost at 17 hours.

2. The test substance was not technical grade or purer. The test substance was specified as "commercial grade"; the purity was not reported. Subdivision N guidelines require that the test substance be technical grade or purer.
3. The test solutions were analyzed for only two degradates, formaldehyde and the thiocyanate ion, at only one or two sampling intervals. The pH 7 test solution was only analyzed at 23 hours posttreatment and pH 9 test solution was only analyzed at 265 minutes and 445 minutes posttreatment. At all remaining sampling intervals, the test solutions were only analyzed for parent vedexil.
3. For the pH 7 and 9 solutions, samples were not analyzed immediately following treatment; rather the first sampling interval was 15 minutes for the pH 7 solution and 10 minutes for the pH 9 solution.
4. The starting concentrations of vedexil (252-263 ug/mL) were slightly in excess of the 250 ppm maximum stated by the Subdivision N guidelines.
5. Recovery efficiencies for fortified samples and method detection limits were not provided.
6. The study authors stated that during the study, the pH of the pH 7 buffer solution was 6.2 at 72 hours and 5.9 at 144 hours. Apparently, the sterility of the solution was not verified at the end of the experiment.

STUDY AUTHOR(S) 'S RESULTS AND/OR CONCLUSIONS  
(INCLUDING PERTINENT TABLES AND FIGURES)



RIN 6245-93

REVIEW ON METHYLENE(BIS)THIOCYANATE

Page \_\_\_\_\_ is not included in this copy.

Pages 17 through 34 are not included.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
- Identity of product impurities.
- Description of the product manufacturing process.
- Description of quality control procedures.
- Identity of the source of product ingredients.
- Sales or other commercial/financial information.
- A draft product label.
- The product confidential statement of formula.
- Information about a pending registration action.
- FIFRA registration data.
- The document is a duplicate of page(s) \_\_\_\_\_.
- The document is not responsive to the request.

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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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DATA EVALUATION RECORD

STUDY 2

CHEM 068102

Vedexil

§161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41897101

Cameron, B.D., B.E. Hall, and M. Phillips. 1991. Artificial sunlight photodegradation of [<sup>14</sup>C]-MTC in buffered aqueous solution. IRI Project No. 380228. Unpublished study performed by Inveresk Research International, Tranent, Scotland, and submitted by Buckman Laboratories, Memphis, TN.

DIRECT REVIEW TIME = 10

REVIEWED BY: L. Parsons TITLE: Staff Scientist

EDITED BY: W. Martin TITLE: Staff Scientist  
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TEL: 703-305-5025

SIGNATURE: *M. Shamim*

CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is unacceptable and cannot be used to fulfill data requirements at this time.
2. Vedexil photodegraded slowly in a sterile pH 5 buffer solution at 23.8-26 C irradiated with an artificial light source (xenon lamp). Vedexil comprised 70% of the recovered radioactivity after 372 hours of irradiation. Two uncharacterized degradates were isolated.
3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reason:

two degradates, isolated at maximums of 7.25-12.88% and 16.86-20.21% of the extracted radioactivity, were not characterized.

4. In order for this study to fulfill the photodegradation in water data requirement, the two uncharacterized degradates must be identified.

#### METHODOLOGY:

Methyl-labeled [<sup>14</sup>C]vedexil [methylene-bis(thiocyanate) (MTC), radiochemical purity >98%, specific activity 90.80 uCi/mg, Sigma Chemical Company] plus unlabeled vedexil were dissolved in sterile pH 5 buffer (0.1 M potassium hydrogen phthalate:0.1 M sodium hydroxide:water, 10:4.52:5.48) at a nominal concentration of 240 ppm. The solution was filter-sterilized (0.22 um) and aliquots were transferred into sterile glass vessels with quartz covers. The vessels were irradiated with a xenon light source (Heraeus Suntest CPS) on a 12-hour photoperiod at 23.8-26.0 C; a UV filter removed wavelengths <290 nm. Additional aliquots of the test solution were transferred to amber glass vessels and were wrapped in aluminum foil to serve as dark controls; the dark controls were maintained at 20.2-27.0 C in a water bath. For 15 minutes prior to each sampling interval, the vessel to be sampled was connected to an air-flow system. Filtered, humidified CO<sub>2</sub>-free air was pumped into the vessels and exhausted sequentially through an ORBO<sup>®</sup>-24 trapping solution (specifically for formaldehyde), and then through water, ethanediol, and ethanolamine trapping solutions. Samples were removed after 48, 96, 180, 264, and 372 hours of irradiation (84, 180, 348, 516, and 732 hours of incubation, respectively). Trapping solutions were changed weekly or at each sampling interval; the tubes containing the ORBO<sup>®</sup>-24 solution were removed for analysis at each sampling interval.

Aliquots of both solutions (irradiated and dark control) were analyzed for total radioactivity by LSC. Additional aliquots of both solutions were analyzed by HPLC using a Spherisorb ODS 2 column eluted with water:methanol (80:20, v:v) and radioactivity detection. The irradiated and dark control vessels were filled with acetone and soaked overnight; the acetone washes were analyzed by LSC. Aliquots of the trapping solutions were analyzed by LSC. The ORBO<sup>®</sup>-24 trapping solutions were extracted with toluene and the toluene extract was analyzed by LSC.

#### DATA SUMMARY:

Methyl-labeled [<sup>14</sup>C]vedexil (radiochemical purity >98%), at a nominal concentration of 240 ppm, photodegraded slowly in sterile aqueous buffered (pH 5) solutions that were irradiated with an artificial light source (xenon light) at 23.8-26.0 C. After 372 hours of irradiation (732 hours of incubation), parent vedexil comprised 68.21-73.81% of the extracted radioactivity in the irradiated samples

and 91.97-99.01% of the extracted radioactivity in the dark controls (Tables 4 and 5). Two unidentified degradates, present in the irradiated samples, comprised 7.25-12.88% ( $R_f$  152-168 seconds) and 16.86-20.21% ( $R_f$  206-222 seconds) of the extracted radioactivity (Table 4). During the study, the test solutions (both irradiated and dark controls) contained 92.35-105.78% of the applied radioactivity, the rinsates from the photolysis vessels comprised 0.01-0.44%, and the trapping solutions comprised  $\leq 0.05\%$  (Tables 2 and 3).

The total irradiance after 732 hours of incubation was 163584-163776  $\text{Whm}^{-2}$ ; the mean daily irradiance was 4800-5283  $\text{Whm}^{-2}$ . The material balances were 92.4-102.43% of the applied radioactivity in the irradiated solutions and 95.91-105.81% in the dark control solutions (Tables 2 and 3).

#### COMMENTS:

1. Two degradates, with HPLC retention times of 152-168 and 206-222 seconds, were isolated from the irradiated solution at maximum percentages of 12.88% and 20.21% of the extracted radioactivity, respectively. Subdivision N guidelines state that all degradates present at  $\geq 10\%$  of the applied must be identified.
2. In a preliminary experiment, there was a major discrepancy between the reviewer-calculated concentration of vedexil in the solution (251 ppm) and the amount measured by LSC (159 ppm). For the definitive study, the authors state that "the concentration was calculated to be 240 ppm". It is unclear if this value refers to the nominal concentration (prior to filtration) or was calculated from the results of LSC analysis of the sterile solution.
3. The absorbance spectrum of vedexil in the test solution was not provided.
4. EFGWB prefers that [ $^{14}\text{C}$ ]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the  $R_f$  of reference standards.

In this study, the sample extracts were analyzed using HPLC eluted with one solvent system. Apparently, the identity of [ $^{14}\text{C}$ ]vedexil was confirmed by comparison of retention times with unlabeled vedexil standard. Although the study protocol states that the degradates will be cochromatographed with suitable standards, the study author stated "Putative degradates were not available for chromatographic comparison with these photoproducts."

RIN 6245-93

REVIEW ON METHYLENE (BIS) THIOCYANATE

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Pages 38 through 46 are not included.

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- Identity of product inert ingredients.
- Identity of product impurities.
- Description of the product manufacturing process.
- Description of quality control procedures.
- Identity of the source of product ingredients.
- Sales or other commercial/financial information.
- A draft product label.
- The product confidential statement of formula.
- Information about a pending registration action.
- FIFRA registration data.
- The document is a duplicate of page(s) \_\_\_\_\_.
- The document is not responsive to the request.

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DATA EVALUATION RECORD

STUDY 3

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CHEM 068102

Vedexil

§163-1  
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FORMULATION--00--ACTIVE INGREDIENT  
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STUDY ID 41764601

Cameron, B.D., B.E. Hall, and R. Jackson. 1990. The adsorption and desorption characteristics of [<sup>14</sup>C]-MTC in soil. IRI Project No. 380212. Report No. 7439. Unpublished study performed by Inveresk Research International, Tranent, Scotland, and submitted by Buckman Laboratories, Memphis, TN.  
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DIRECT REVIEW TIME = 5  
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REVIEWED BY: J. Harlin

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EDITED BY: L. Mickley  
W. Martin

TITLE: Staff Scientist  
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TEL: 703-305-5025

SIGNATURE: *M. Shamim*

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is unacceptable and cannot be used to fulfill data requirements.
2. Based on batch equilibrium experiments, vedexil is very mobile in sand, sandy loam, silt loam, and silty clay soils, with Freundlich  $K_{ads}$  values of 0.3934-0.8140.
3. This study is scientifically sound but does not meet Subdivision N guidelines for the following reason:

the adsorption of vedexil to the soil was determined only by the decrease in concentration of vedexil in the supernatant. The soils were not analyzed following adsorption or desorption to provide complete material balance;

no other analytical method, beside LSC, was used to confirm the presence of parent vedexil or its degradates in the supernatant.

4. Since the soils were not analyzed to confirm adsorption and to complete material balance and since other analytical techniques such as HPLC and GC were not used to confirm the presence of parent vedexil or its degradates in the supernatants, the problems with this study cannot be resolved with submission of additional data. A new study must be submitted.

#### METHODOLOGY:

Sand, sandy loam, silt loam, and silty clay soils (Appendix 3) were oven-dried and sieved (2-mm). Based on preliminary batch equilibrium experiments, a 2-hour equilibration time and a 1:5 soil:solution ratio were selected for the definitive experiment.

Methyl-labeled [ $^{14}\text{C}$ ]vedexil (radiochemical purity >98%, specific activity 13.1 mCi/mMol, Sigma Chemical Company) plus unlabeled vedexil (purity not reported) were dissolved at nominal concentrations of 0.1, 0.2, 0.5, and 1.0 mg/mL in a 0.01 M  $\text{CaCl}_2$  solution. Duplicate soil subsamples (2 g) and aliquots (10 mL) of the treated solutions were placed in screw-capped glass tubes. The soil:solution slurries were equilibrated on a wrist-action shaker in the dark (temperature unspecified) for 2 hours. Following equilibration, the soil:solution slurries were centrifuged and the supernatant were decanted; duplicate aliquots of the supernatant were analyzed by LSC. The amount of vedexil adsorbed to the soil was determined by subtraction of background count rates from sample count rates.

To determine desorption potential, the decanted supernatant was replaced with an equivalent amount of pesticide-free 0.01 M  $\text{CaCl}_2$  solution. The soil:solution slurries were equilibrated by shaking on a wrist-action shaker for 2 hours (temperature unspecified) in the dark, and then centrifuged. Duplicate aliquots of the supernatant were removed and analyzed by LSC.

#### DATA SUMMARY:

Based on batch equilibrium studies, methyl-labeled [ $^{14}\text{C}$ ]vedexil (radiochemical purity >98%), at nominal concentrations of 0.1, 0.2, 0.5, and 1.0 mg/mL, was very mobile in sand, sandy loam, silt loam, and silty clay soil: $\text{CaCl}_2$  (1:5) slurries that were incubated in the dark (temperature unspecified) for 2 hours. Freundlich  $K_{\text{ads}}$  values

were 0.8140 for the silty clay soil, 0.4836 for the silt loam soil, 0.4447 for the sand soil, and 0.3934 for the sandy loam soil; respective  $K_{oc}$  values were 166.1, 86.36, 38.67, and 43.23 (Table 4).

Following desorption, 89.68-92.64% of the applied radioactivity remained in solution (Table 5).  $K_{des}$  values were 2.737 for the silty clay soil, 3.274 for the silt loam soil, 3.422 for the sand soil, and 2.913 for the sandy loam soil (Table 4).

COMMENTS:

1. The temperature at which the study was conducted was not reported.
2. The soils were not analyzed after equilibration to confirm adsorption and to provide a complete material balance. The adsorption of vedexil to the soil was determined only by the decrease in concentration in the supernatant. Material balances of 89.68-92.64% of the applied were based on the concentration of vedexil in solution following desorption.
3. The preliminary experiment conducted to determine equilibration time was conducted using the sand soil. The study authors reasoned that the sand soil would have the least adsorption of the test material and the longest equilibrium time, since the sand soil contained the lowest clay and organic matter contents.
4. A preliminary experiment indicated that [ $^{14}\text{C}$ ]vedexil did not adsorb to the glass surface of the test tubes; >97% of the applied remained in solution after 24 hours.
6. Recovery efficiencies and method detection limits were not reported.



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REVIEW ON METHYLENE(BIS)THIOCYANATE

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Pages 50 through 57 are not included.

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- Identity of product inert ingredients.
- Identity of product impurities.
- Description of the product manufacturing process.
- Description of quality control procedures.
- Identity of the source of product ingredients.
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- FIFRA registration data.
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- The document is not responsive to the request.

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## REFERENCES

The following studies were reviewed:

Macdonald, I.A. and D.A. Howes. 1985. The determination of the hydrolysis of methylene bis thiocyanate as a function of pH. HRC Project No. A & W 460/85626. Unpublished study performed by Huntington Research Centre Ltd., Cambridgeshire, England, and submitted by Buckman Laboratories, Memphis, TN. (150229)

Cameron, B.D., B.E. Hall, and M. Phillips. 1991. Artificial sunlight photodegradation of [<sup>14</sup>C]MTC in buffered aqueous solution. IRI Project No. 380228. Unpublished study performed by Inveresk Research International, Tranent, Scotland, and submitted by Buckman Laboratories, Memphis, TN. (41897101)

Cameron, B.D., B.E. Hall, and R. Jackson. 1990. The adsorption and desorption characteristics of [<sup>14</sup>C]-MTC in soil. IRI Project No. 380212. Report No. 7439. Unpublished study performed by Inveresk Research International, Tranent, Scotland, and submitted by Buckman Laboratories, Memphis, TN. (41764601)

Environmental Fate & Effects Division  
 PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY  
 METHYLENE BIS(THIOCYANATE)

Last Update on December 9, 1991

[V] = Validated Study    [S] = Supplemental Study    [U] = USDA Data

LOGOUT	Reviewer:	Section Head: <i>Q</i>	Date: JAN 2 1992
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Common Name: METHYLENE BIS(THIOCYANATE)

PC Code # : 68102      CAS #: 6317-18-6      Caswell #:

Chem. Name : METHYLENE BIS(THIOCYANATE)

Action Type: Microbiocide (bactericide)

Trade Names: VEDEXIL

(Formul'tn): ACTIVE INGREDIENT METHYLENE-BIS(THIOCYANATE)

Physical State: SOLID

Use : TERRESTRIAL NONFOOD  
 Patterns : AQUATIC NONFOOD  
 (% Usage) : INDOOR/OUTDOOR RESIDENTIAL  
               : INDOOR FOOD/NONFOOD

Empirical Form:  $C_3H_2S_2N_2$   
 Molecular Wgt.: 130.18      Vapor Pressure: 1.22E -4 Torr  
 Melting Point : 105-107 C °C      Boiling Point: °C  
 Log Kow : <1      pKa: e °C  
 Henry's : E      Atm. M3/Mol (Measured) 7.46E -9 (calc'd)

Solubility in ...					Comments
Water	2.80E	3	ppm	@25.0 °C	
Acetone	E		ppm	@ °C	
Acetonitrile	E		ppm	@ °C	
Benzene	E		ppm	@ °C	
Chloroform	E		ppm	@ °C	
Ethanol	E		ppm	@ °C	
Methanol	E		ppm	@ °C	
Toluene	E		ppm	@ °C	
Xylene	E		ppm	@ °C	
	E		ppm	@ °C	
	E		ppm	@ °C	

Hydrolysis (161-1)  
 [S] pH 5.0: STABLE  
 [S] pH 7.0: 21.5 HR  
 [S] pH 9.0: 2.2 HR  
 [ ] pH :  
 [ ] pH :  
 [ ] pH :

59

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Photolysis (161-2, -3, -4)

[ ] Water:  
[ ] :  
[ ] :  
[ ] :

[ ] Soil :  
[ ] Air :

Aerobic Soil Metabolism (162-1)

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Anaerobic Soil Metabolism (162-2)

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Anaerobic Aquatic Metabolism (162-3)

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Aerobic Aquatic Metabolism (162-4)

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Soil Partition Coefficient (Kd) (163-1)

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Soil Rf Factors (163-1)

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Laboratory Volatility (163-2)

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Field Volatility (163-3)

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Terrestrial Field Dissipation (164-1)

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Aquatic Dissipation (164-2)

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Forestry Dissipation (164-3)

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Long-Term Soil Dissipation (164-5)

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Accumulation in Rotational Crops, Confined (165-1)

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Accumulation in Rotational Crops, Field (165-2)

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Accumulation in Irrigated Crops (165-3)

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Bioaccumulation in Fish (165-4)

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Bioaccumulation in Non-Target Organisms (165-5)

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Ground Water Monitoring, Prospective (166-1)

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Ground Water Monitoring, Small Scale Retrospective (166-2)

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Ground Water Monitoring, Large Scale Retrospective (166-3)

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Ground Water Monitoring, Miscellaneous Data (158.75)

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Field Runoff (167-1)

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Surface Water Monitoring (167-2)

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Spray Drift, Droplet Spectrum (201-1)

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Spray Drift, Field Evaluation (202-1)

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Degradation Products

Formaldehyde (neut. & alkaline hydrol.)  
Thiocyanate ion (neut. & alkal. hydrol.)

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Comments

References: EPA REVIEWS  
Writer : MTS