1-13-88

Shaughnessy No: 109702

Date Out of EAB: JAN 13 1988

To: George LaRocca
Product Manager #15
Registration Division (TS-767C)

From: Michael Firestone, Chief
Special Review Section
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Thru: Paul F. Schuda, Chief
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Attached, please find the EAB review of:

Reg./File # : 279-3026/3027

Chemical Name : Cypermethrin

Type Product : Insecticide

Product Name : Ammo

Company Name : FMC Corporation

Purpose : Review of Air Monitoring Data

Date Received : 1/21/87 Action Code: 405

Date Completed: _____ EAB #(s): 70204-5

Monitoring study requested: _____ Total Reviewing Time: 5 days

Monitoring study voluntarily: X

Deferrals to: _____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1/9

[redacted]

JAN 13 1988

MEMORANDUM

SUBJECT: Airborne HCN Liberated From Cypermethrin

FROM: David Jaquith
Special Review Section
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

TO: George LaRocca
Product Manager 15
Registration Division (TS-769C)

THRU: Michael Firestone, Chief
Special Review Section
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

THRU: Paul Schuda, Chief
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

EAB has been requested by Toxicology Branch (TB) to evaluate a report by FMC Corporation addressing air levels of hydrogen cyanide (HCN) in the air of rooms containing their insecticide cypermethrin (Ammo Technical Insecticide EPA Reg. No.279-3027). The registrant had previously informed the Agency that detectable amounts of HCN could be found in the headspace of containers of this product. In a previous review of this information by TB, it was determined that the levels of HCN were below those which would be expected to result in a hazard. The registrant later reported that the original measured levels of HCN were inaccurate due to an error in the analytical methodology. The concentrations would actually be expected to be 15 times lower than that previously reported, based on equilibrium studies. EAB has been requested to evaluate the chemical methodology and exposures from various actual and simulated circumstances.

CONCURRENCES								
SYMBOL	EAB	EAB	TS769C					(2)
SURNAME	Jaquith	LEWIS	Schuda					
DATE	1/12/88	1/13/88	1/22/88					

EPA Form 1320-1 (12-70)

OFFICIAL FILE COPY

DESCRIPTION OF STUDIES

Evaluation of Commercial HCN Detectors

There are several commercially available detector tubes for measuring HCN in the workplace. The registrant generated an atmosphere containing 15 ul of HCN per liter. Gas samples of 100 ml were removed from the flask using either a Gastec or MSA sampler. The results of these tests are presented in Table 1.

Table 1. Comparison of the Results of Measurement of Air Samples Containing HCN (15 ul/L) Using Two Different Measuring Devices.

Gastec Tube	MSA Tube
19	10
17	7
20	7
19.5	

The Gastec tubes consistently overestimated the actual concentrations in the chamber with the average value exceeding the standard by 27 percent. The results obtained from such tubes would therefore be conservative. The registrant has also been evaluating other measurement techniques such as Draeger tubes, ion selective electrodes, and gas chromatography. The results of these studies have not been submitted to the Agency.

Liquid-Vapor Phase Equilibrium Studies

The registrant submitted a theoretical equilibrium model that showed that the headspace concentration of HCN varies with the ratio of the headspace volume to the mass of the liquid phase when the amount of HCN is held constant. The derivation of this model is presented in Appendix A. An equilibrium experiment was then conducted. A weighed sample of the insecticide was placed in a saturator. The atmosphere in the saturator was circulated for several hours to achieve equilibrium. The amounts of HCN in both the liquid and vapor phases were then measured. The distribution coefficient (K) of HCN between the vapor (ul/L) and the associated liquid phase (ug/g) was found to be 15 for Ammo 2.5 EC. The technical material was too viscous to allow sufficient nitrogen flow in the saturator but it was expected that the K value for this material would be higher.

Further investigations to determine the potential for hydrogen cyanide liberation from the formulated product were conducted in the spring and summer. Monitoring of airborne concentrations

of HCN was conducted during transfer of technical material, rinsing of the technical drums, product mixing, and packing. Samples were also taken during warm room storage of the product. Measurements were taken using Gastec or MSA tubes and by continuous monitoring with a HCN detector with a minimum detection limit of 1 ppm. Test measurements taken from the numerous sources. The results of these samples are presented in Table 2.

CONCLUSIONS

The registrant has submitted data measuring the concentration of HCN in the air of enclosed areas containing cypermethrin. The data presented supports the theoretical model described in Appendix A. The data should be adequate to allow Toxicology Branch to determine any hazards to persons in contact with these atmospheres.

Table 2. Results of Sampling for HCN in Drum Headspace, Formulating Work Areas, and Under Simulated Spill Conditions.

Description of Sample	HCN Concentration (ppm)
Headspace of Drums at Manufacturing Plant (80 degrees F)	6-15
Headspace of Drums warmed to 41-44 degrees C	40-120
Headspace of Full Containers	40-200
Within 3 inches of bung when collecting samples	1-2
Outside 3 inch perimeter when taking samples	None detected
Worker Samples during undrumming and rinsing of drums	None detected
Simulated spill, 1000 cubic ft, 30 gal. Ammo 2.5 EC, Vh = 92	22-30
Simulated spill, 2560 cubic ft, 30 gal. Ammo 2.5 EC, Vh = 92	8-15
Simulated spill, 2560 cubic ft, 30 gal. Ammo 2.5 EC, Vh = 29	Trace to 1.5
Simulated spill, 2560 cubic ft, 55 gal. Ammo 2.5 EC, Vh = 68	2-7
Simulated spill, 14400 cubic ft, 30 gal. Ammo 2.5 EC, Vh = 92	Less than 1
Simulated spill, 14400 cubic ft, 55 gal. Ammo 2.5 EC, Vh = 68	Less than 1

Appendix A. Derivation of a Model to Predict the Airborne Concentration of HCN in Equilibrium with Liquid Cypermethrin.

Assume a closed system containing HCN in both the liquid and vapor phases. Let:

m = mass of the liquid phase

V_h = Volume of the headspace

C_l = micrograms of HCN per gram of the liquid phase or ppm (w/w)

C_h = microliters of HCN per liter in the vapor phase or ppm (v/v)

Q_o = Total mass (ug) of HCN in the system

$$Q_o = mC_l + 27.03 \text{ g HCN/mol HCN} \times \frac{1 \text{ mol HCN}}{24.46 \text{ l at 25 C, 1 atm}} \times V_h \times C_h$$

$$= mC_l + 1.105\ V_hC_h$$

Henry's Law states that the concentration of a gas dissolved in a liquid will be directly proportional to the pressure of the gas in equilibrium with the liquid. The proportionality for this calculation is:

$$K = \frac{C_h}{C_l}$$

Rearranging, substituting and solving for Q_o gives:

$$Q_o = m(C_h/K) + 1.105\ V_hC_h$$

$$= C_h(m/K + 1.105\ V_h)$$

$$KQ_o = C_h(m + 1.105\ V_hK$$

$$C_h = \frac{KQ_o}{m + 1.105\ V_hK}$$

or,

$$C_h = \frac{KQ_o}{1 + 1.105\ KV_h/m}$$

If the "headspace" is increased, such as the case if a container is spilled in a room:

Letting V = the new volume of the vapor phase and C_v = the concentration of HCN in the new volume, and since Q_o is constant:

$$C_h(m/K + 1.105\ V_h) = C_v(m/K + 1.105\ V)$$

solving for C_v gives:

$$C_v = C_h \times \frac{1 + 1.105\ KV_h/m}{1 + 1.105\ KV/m}$$

Suppose the contents of a 55 gallon drum of Ammo 2.5 EC are spilled in a room with dimensions 40 ft x 20 ft x 20 ft and the volume of the original headspace is 7 liters. Using a K of 15 as determined by experiment:

The above equation becomes:

$$C_v = C_h \times \frac{1 + 16.5\ V_h/m}{1 + 16.5\ V/m}$$

if the headspace is 7 L:

$$C_v = \frac{C_h}{1 + 7.9 \times 10^{-5}\ V}$$

$m = 55\ gal \times 8.4\ lb/gal \times 454\ g/lb$

$= 2.1 \times 10^5\ g$

$V = 40\ ft \times 20\ ft \times 20\ ft \times 28.3\ L/cu\ ft$

$= 4.5 \times 10^5\ L$

Substituting and solving the above equation gives:

$$C_v = C_h/36.8$$

For example, at room temperature, if the headspace of the drum had a concentraion of 50 ul/L before the spill, the room air would contain 1.4 ul/L at equilibrium.

ATTN: Dr. Joseph C. Reinert

REGISTRATION DIVISION DATA REVIEW RECORD

Confidential Business Information – Does Not Contain National Security Information (E.O. 12065)

1991 #2

1-22-87

1. CHEMICAL NAME: CYPERMETHRIN - TC Referral regarding Exposure Method

2. IDENTIFYING NUMBER	3. ACTION CODE	4. ACCESSION NUMBER
279-3026/3027	405	N/A
Please Respond Within	30 DAYS	
or Sooner		

TO BE COMPLETED BY PM

5. RECORD NUMBER: 188071

6. REFERENCE NUMBER: 2

7. DATE RECEIVED (EPA): 1.20.87

8. STATUTORY DUE DATE:

9. PRODUCT MANAGER (PM): LaRocca / 04

10. PM TEAM NUMBER: 15

14. CHECK IF APPLICABLE

- ☐ Public Health/Quarantine
- ☐ Minor Use
- ☐ Substitute Chemical
- ☐ Part of IPM
- ☒ Seasonal Concern
- ☐ Review Requires Less Than 4 Hours

AH

TO BE COMPLETED BY PCB

11. DATE SENT TO HED/TSS: 1-21-87

12. PRIORITY NUMBER: 1

13. PROJECTED RETURN DATE: 2-19-87

15. INSTRUCTIONS TO REVIEWER

A. HED
- ☐ Total Assessment - 3(c)(5)
- ☐ Incremental Risk Assessment - 3(c)(7) and/or E.L. Johnson memo of May 12, 1977.

B. SPRD (Send Copy of Form to SPRD PM)
- ☐ Chemical Undergoing Active RPAR Review
- ☐ Chemical Undergoing Active Registration Standards Review

C. ☐ BFSD

D. ☐ TSS/RD

E. ☒ Other

F. INSTRUCTIONS

Refer to the attached "TC" review and the attached information. Please give your opinion regarding the buildup of HCN and the Chemical Methods used to quantitate for hydrogen cyanide or the exposure resulting from various "actual and simulated" circumstances.

16. RELATED ACTIONS

17. 3(c)(1)(D)
- ☒ Use Any or All Available Information
- ☐ Use Only Attached Data
- ☐ Use Only the Attached Data for Formulation and Any or All Available Information on the Technical or Manufacturing Chemical:

18. REVIEWS SENT TO
- ☐ TB
- ☐ EEB
- ☐ EF
- ☐ PL
- ☐ RCB
- ☒ EFB
- ☐ CH
- ☐ BFSD

19.	To	TYPE OF REVIEW	NUMBER OF ACTIONS: Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
HED		TOXICOLOGY								
		ECOLOGICAL EFFECTS								
		RESIDUE CHEMISTRY								
	1	ENVIRONMENTAL DATE	1							
RD/TSS		CHEMISTRY								
		EFFICACY								
		PRECAUTIONARY LABELING								
BFSD		ECONOMIC ANALYSIS								(8)

20.	21.	22.	23.	24.
☐ Label Submitted with Application Attached	☐ Confidential Statement of Formula	☐ Representative Labels Showing Accepted Uses Attached	Date Returned to RD (to be completed by HED)	Include an Original and 4 (four) Copies of This Completed Form for Each Branch Checked for Review.

ATTN: Dr. Joseph C. Reinert

REGISTRATION DIVISION DATA REVIEW RECORD

19913 HQ

Confidential Business Information — Does Not Contain National Security Information (E.O. 12065) 1-22-87

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CYPERMETHRIN - TB Referral (regarding Exposure Method)

2. IDENTIFYING NUMBER	3. ACTION CODE	4. ACCESSION NUMBER
279-3026/3027	405	N/A
Please Respond Within or Sooner	30 DAYS	

TO BE COMPLETED BY PM

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E. ☒ Other

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19.	To	TYPE OF REVIEW	NUMBER OF ACTIONS: Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
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HED	1	ENVIRONMENTAL DATE	1							
RD/TSS		CHEMISTRY								
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RD/TSS		PRECAUTIONARY LABELING								
BFSD		ECONOMIC ANALYSIS								(9)

20.	21.	22.	23.	24.
☐ Label Submitted with Application Attached	☐ Confidential Statement of Formula	☐ Representative Labels Showing Accepted Uses Attached	Date Returned to RD (to be completed by HED)	Include an Original and 4 (four) Copies of This Completed Form for Each Branch Checked for Review.