



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

FEB 22 1990

FEB 22 1990

**MEMORANDUM**OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

**SUBJECT:** PP#9E3791. Cyromazine in/on Chinese Mustard.  
Evaluation of Analytical Methods and Residue Data.  
DEB No. 5695; RD Record No. 249458,  
HED Project No. 9-1985A. MRID No. 411930-00.01

**FROM:** Luis F. Rodriguez, Ph.D., Chemist. *Luis Rodriguez*  
Tolerance Petition Section II,  
Dietary Exposure Branch,  
Health Effects Division. (H7509C).

**THROUGH:** Debra F. Edwards, Ph.D., Section Head. *Debra Edwards*  
Tolerance Petition Section II,  
Dietary Exposure Branch,  
Health Effects Division. (H7509C).

**TO:** Hoyt Jamerson, PM #43  
Minor Uses Officer  
Registration Division (H7505C).

**Background:**

Dr. W. L. Biehn, Associate Coordinator, and  
Dr. R. H. Kupelian, National Director of The Interregional  
Project 4 (IR-4), State Agricultural Experiment Station, Rutgers  
University, New Brunswick, NJ, on behalf of IR-4 project, and the  
Agricultural Experiment Station of Florida are requesting the  
establishment of a tolerance for the residues of the pesticide  
chemical cyromazine, N-cyclopropyl-1,3,5-triazine-2,4,6-triamine,  
and its metabolite melamine, 1,3,5-triazine-2,4,6-triamine,  
calculated as cyromazine in or on the raw agricultural commodity  
chinese mustard at 5.0 ppm.

A letter of authorization written by Kim Dawson, Associate  
Regulatory Specialist, CIBA-GEIGY Corp, on 7/19/89 is submitted.  
It authorizes the Registration Division to refer to all  
cyromazine data which are considered necessary to support this  
IR-4 petition.

Tolerances have been established in 40 CFR 180.414 for  
residues of cyromazine in or on eggs (0.25 ppm), poultry and  
poultry byproducts (0.05 ppm), lettuce, head (5.0 ppm), and  
celery (10 ppm).

**BEST COPY AVAILABLE**

564

**DEB's Conclusions/Comments:**

1. The nature of the residue in plants is considered adequately understood for the purpose of this proposed use on chinese mustard. The residues of concern are cyromazine and its metabolite melamine.
2. There are no feed items associated with the proposed use on chinese mustard. No secondary residues are expected. Therefore, the nature of the residue in livestock is not relevant to this petition.
3. Adequate enforcement methods are available in PAM II. However, cyromazine and melamine must be checked to determine if they are recovered by FDA Multiresidue methods. The registrant has been asked to provide these data (see memo of J. B. Stokes, 11/10/88).
4. Based on the available residue data, DEB considers that the proposed tolerance will not allow for the detection of misuse of the pesticide, and that a lower tolerance of 3 ppm will be more adequate. The petitioner must submit a revised section F proposing a more adequate tolerance.
5. The storage stability of cyromazine is considered adequate to support the residue data submitted. Cyromazine has been shown to be stable under frozen storage conditions for up to 24 months.
6. There are no Canadian, Mexican, or Codex tolerances for cyromazine in/on chinese mustard. Therefore, there are no compatibility problems associated with this petition.

**DEB's Recommendations:**

DEB recommends against the establishment of the proposed tolerance for the residues of cyromazine and its metabolite melamine, in/on chinese mustard at 5.0 ppm due to conclusion 4.

### Detailed Considerations:

#### Manufacture and Formulation:

The manufacture process and formulation of the technical cyromazine (TGAI is 95% pure) have been previously reviewed in detail in connection with PP#9G2230 (see memo of A. Rathman, 11/14/79). The impurities are not likely to produce residue problems. The inert ingredients are cleared for use under §180.1001. The proposed formulation is Trigard 75W Insecticide (EPA Reg. No. 100-654) a wettable powder containing 75% a.i. w/w.

CIBA-GEIGY has submitted results from nitrosamine analysis for cyromazine in which no nitrosamines were detected. DEB found these data valid (see memo of K.W. Dockter, 1/27/89).

#### Proposed Use:

The proposed label is restricted to use in Florida only.

For leafminer control, 1/6 lb/A of Trigard 75W (0.125 lb a.i./A) is to be applied as a foliar spray with ground equipment in a minimum of 5 gal. of water to obtain uniform coverage. The insecticide should be applied when leafminers first appear and applications repeated at seven days intervals or as necessary to maintain control. The maximum number of applications is seven. A pre-harvest interval (PHI) of 7 days is to be observed.

#### Nature of the Residue:

##### Plant Metabolism:

No new metabolism studies are submitted with this petition. Metabolism data have been previously submitted and reviewed in conjunction with other petitions for RACs celery, lettuce and tomatoes (PP#5FG3176, see memo of E. T. Haerberer, 2/4/85; and PP#5F3180, see memos of C. Deyrup, 2/8/85 and 2/20/85).

DEB considers the nature of the residue adequately understood for the purpose of this proposed use on chinese mustard. The residues of concern are the parent compound and its metabolite, melamine.

#### Meat, Milk, Poultry and Eggs:

No livestock metabolism studies have been submitted with this petition.

There are no feed items associated with chinese mustard. Therefore, livestock metabolism studies are not relevant to the purpose of this petition.

#### Methodology:

The residue data submitted were generated using CIBA-GEIGY Method 408, based in a method entitled GC Determination of Cyromazine and its Degradation Product, Melamine, in Chinese Cabbage. (JAOAC, Vol. 70, No. 3, pp. 455-457, 1987). Samples are extracted with methanol-water (95+5) under reflux conditions followed by removal of methanol by rotary evaporation. The aqueous phase, made acidic with HCl, is washed successively with dichloromethane and hexane. The acid aqueous phase is further cleaned up by selective sorption of cyromazine and melamine on a disposable solid phase extraction column, desorption with ammoniacal methanol, and reconstitution in methanol. Analysis of samples was performed on a liquid chromatograph with UV detection at 215 nm. This represents a modification of the original method in which the determinative step involved GC of the analytes.

The limit of detection reported for the determination of cyromazine and melamine in/on chinese mustard is 0.1 ppm. Recoveries for cyromazine fortified at 0.1-3.0 ppm were 72-100%. Recoveries for melamine fortified at 0.10-1.00 ppm were 79-133%.

Adequate enforcement methods are available in PAM II. However, cyromazine and melamine must be checked using FDA Multiresidue methods. The registrant has been asked to provide these data (see memo of J. B. Stokes, 11/10/88).

Residue Data:

A field trial was conducted in Florida with cyromazine on chinese mustard in order to obtain treated crop samples for residue analysis. The samples were immediately frozen and stored at -30 °C until analyzed.

Chinese mustard was treated with 7 applications of cyromazine at dosages of 0.125 lb. a.i./A (1x) and 0.25 lb. a.i./A (2x). Crop samples were harvested 7 and 14 days after the last application and analyzed for cyromazine and its metabolite melamine. The data are summarized in Tables 1 and 2, and show that at the 1x dosage rate, the residue levels for the 14 day PHI samples were higher than the residue levels for the 7 day PHI samples. The petitioner claims that the 7 and 14 day samples may have been switched. Previously submitted data in connection with PP#9E3752 (see memo of W.T. Chin, 12/4/89) show lower residues for a 14 day PHI at a 2x application rate for Bok Choy, which seems to support this possibility.

The maximum residues reported at the 1x rate were 2.910 ppm for cyromazine and 0.544 ppm for melamine (for a combined total of 3.454 ppm). At the 2x rate the maximum residues found were 5.195 ppm for cyromazine and 0.620 ppm for melamine (total of 5.815 ppm).

The residue data reflect less than the proposed 5.0 ppm tolerance level when the product is applied according to the proposed use. However, only one sample exceeds 3 ppm (3.45 ppm) and the average residue for samples representing the maximum proposed rate and minimum PHI was  $2.7 \pm 0.3$  ppm. In addition, a tolerance of 5.0 ppm will not allow for detection of misuse of the pesticide, since most of the samples reflecting a 2x application showed residues below 5.0 ppm. Therefore, DEB recommends that the petitioner submit a revised section F with a reduced proposed tolerance in/on chinese mustard. DEB suggests a tolerance of 3.0 ppm. This will accommodate all of the residue data reported in this petition with the exception of one value, and will be consistent with a previously recommended tolerance (3 ppm) for chinese cabbage, a very closely related crop (see memo of W.T. Chin, 12/4/89).

TABLE 1

Residues of Cyromazine and Melamine (expressed as cyromazine)  
on Chinese Mustard Resulting from Foliar Applications  
of Cyromazine in Florida.

Dosage: 0.125 lb. a.i./A (1x) No. Applications: 7

Sample*	PHI	Residues (ppm)		
		Cyromazine	Melamine	Total
1A	7	1.420	0.207	1.627
2A	7	1.605	0.216	1.821
3A	7	1.439	0.252	1.691
4A	7	1.681	0.287	1.968
5A	7	1.496	0.190	1.686
6A	7	1.429	0.190	1.619
7A	7	1.263	0.207	1.470
8A	7	1.246	0.207	1.453
1B	14	2.910	0.544	3.454
2B	14	2.255	0.448	2.703
3B	14	2.508	0.360	2.868
4B	14	2.130	0.327	2.457
5B	14	2.179	0.330	2.509
6B	14	2.138	0.298	2.436
7B	14	2.727	0.338	3.065
8B	14	2.487	0.298	2.785

\* Sample numbers are arbitrary and not representative of those assigned in the actual study. The petitioner has stated that samples corresponding to PHI 7 and 14 may have been switched.

TABLE 2

Residues of Cyromazine and Melamine  
on Chinese Mustard Resulting from Foliar Applications  
of Cyromazine in Florida.

Dosage: 0.25 lb. a.i./A (2x) No. Applications: 7

Sample*	PHI	Residues (ppm)		
		Cyromazine	Melamine	Total
1C	7	4.914	0.714	5.628
2C	7	3.534	0.498	4.032
3C	7	5.195	0.620	5.815
4C	7	4.521	0.508	5.029
5C	7	2.278	0.280	2.558
6C	7	3.098	0.378	3.476
7C	7	3.626	0.370	3.996
8C	7	3.375	0.362	3.737
1D	14	2.596	0.518	3.114
2D	14	2.466	0.460	2.926
3D	14	1.360	0.185	1.545
4D	14	2.302	0.310	2.612
5D	14	2.755	0.417	3.172
6D	14	2.792	0.425	3.217
7D	14	3.483	0.401	3.884
8D	14	3.612	0.449	4.061

\* Sample numbers are arbitrary and not representative of those assigned in the actual study.

Storage Stability:

The samples obtained in the Florida field trial were immediately frozen and stored at -30 °C until analyzed. Sample extracts were stored at approximately 4 °C when not in use.

Storage stability data have been previously submitted in conjunction with PP#6F3329 (see memo of A. Smith, 1/28/87). Several field crops (head lettuce, leaf lettuce, celery, mushrooms and tomatoes) were sampled and analyzed for residues of cyromazine and melamine. The samples were stored frozen (-15 °C) for periods of 9 to 24 months. Analyses following frozen storage showed no loss of residues in any of the crops. These studies show that cyromazine residues are stable under frozen storage for up to 24 months.

Storage stability data have been submitted with this petition. Control samples were fortified at 0.5 ppm and 1.00 ppm and frozen for the same period of time the field samples were stored. On the day of analysis, additional control samples were fortified (0.5 ppm) on the day of the analysis for recovery studies. Recoveries obtained for the stored samples averaged 64.5% (0.50 ppm) and 76.7% (1.00 ppm). The control samples fortified on the day of analysis averaged 78.5% recoveries. These studies show that cyromazine is stable for the period of time involved in these residue studies.

DEB considers the storage stability of cyromazine adequate to support the residue data associated with this petition.

Geographic:

This petition proposes a tolerance with regional registration (Florida only). The field residue trials were conducted in FL. Therefore, the geographic representation is considered adequate for this proposed registration.

International Residue Limits:

An IRL Status sheet for cyromazine and its metabolite, melamine, in/on chinese mustard (Bok Choy) is attached.

There are no Canadian, Mexican, or Codex tolerances for cyromazine in/on chinese mustard. Therefore, there are no compatibility problems associated with this petition.

Attachment: Cyromazine IRL Status Sheet

cc: RF, SF, Circ, PP#9E3791, L. Rodriguez, R.D. Schmitt,  
J. Karya (DRES/SACB), PMSD/ISB  
RDI:D.F.Edwards:2/21/90:R.Loranger:2/21/90  
H7509C:DEB:L.Rodriguez:lr:2/22/90:CM#2:RMS00D:557-1669

572

*Jim Rodryg*  
1/24/90

Attachment:

Page 1 of 1

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Cyromazine

CODEX NO. \_\_\_\_\_

CODEX STATUS:

No Codex Proposal  
Step 6 or Above

Residue (if Step 8): \_\_\_\_\_

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
----------------	--------------------------

PROPOSED U.S. TOLERANCES:

Petition No. 9E3791

DER Reviewer L. Rodriguez

Residue: Cyromazine and its  
metabolite melamine\*

\* (1,3,5-Triazine - 2,4,6-Triamine)

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
----------------	--------------------------

Chinese Mustard (BOK CHOY)	5.0 ppm
-------------------------------	---------

CANADIAN LIMITS:

No Canadian Limit

Residue: \_\_\_\_\_

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
----------------	--------------------------

MEXICAN LIMITS:

No Mexican Limit

Residue: \_\_\_\_\_

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
----------------	--------------------------

NOTES

Data based on previous  
IRS sheet in conjunction with 9E3752  
and dated 10/21/89.

Form Revised 1989

573

**BEST COPY AVAILABLE**

10