

**MEMORANDUM**

SUBJECT: PP# 5G04583. Fipronil in/on Cotton. **Request for Petition Method Validation.** MRID#s 437766-04 & -05. Barcode D230789. Chemical No 129121. Case 286984.

FROM: G.F. Kramer, Ph.D., Chemist  
Tolerance Petition Team I  
Chemistry Branch I, Tolerance Support  
Health Effects Division (7509C)

THRU: E.T. Haeberer, Acting Branch Chief  
Chemistry Branch I, Tolerance Support  
Health Effects Division (7509C)

TO: Donald A. Marlow, Chief  
Analytical Chemistry Branch  
Biological and Economics Analysis Division (7503W)

Rhône-Poulenc has submitted an application for temporary tolerances for the insecticide fipronil (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinyl pyrazole) or its metabolites MB 46136 (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonyl pyrazole) or MB 45950 (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthiopyrazole) or MB 46513 (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylpyrazole) on/in cottonseed. The petitioner has proposed the following tolerances for cotton commodities (expressed as parent or metabolites MB 45950 or MB 46136 or MB 46513):

Cottonseed    --- 0.02 ppm    |    Seed processing fractions -- 0.02 ppm

The petitioner has submitted a copy of method EC-95-303 and an Independent Laboratory Validation (ILV) in the following volumes which are appended to this memorandum as Attachments 2 & 3:

Fipronil- Validation of Method of Analysis for Fipronil and Its Metabolites in/on Potato and Cotton Matrices (Excluding Cotton Gin Trash). EC-95-303. MRID# 437766-04. Independent Validation of the Rhône-Poulenc Method Entitled, "Insecticides, Fipronil-Analytical Method for the Determination of Fipronil and Its Metabolites in/on Cotton and Potatoes" Horizon Labs. MRID# 437766-05.

CBTS has conducted a preliminary review of the ILV. Acceptable recoveries were obtained by the laboratory. A summary of the laboratory's findings may be found on page 26 of the ILV report. CBTS requests that ACL conduct a Petition Method Validation (PMV) on the submitted analytical method.

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CBTS is also requesting that the method be validated using metabolite RPA 200766. This metabolite is not currently included in the fipronil tolerance expression but it has been found to be a major metabolite in other plant matrices. The petitioner and the independent lab have also provided validation data for this metabolite.

Samples should be run in duplicate per the experimental design specified in Attachment 1. Please complete and return this attachment as part of your report. Also, please include with your report, copies of the standard curves, sample calculations, and representative chromatograms for controls and fortified samples. Any deficiencies in the method, as written, should also be noted and reported. Please comment on the length of time necessary to complete a set of samples.

One of the purposes of conducting a PMV is to determine whether all necessary instructions are included in the submitted method. For this reason, we are requesting that laboratory staff scientists have minimal contact with the petitioner during this PMV. Any problems encountered should be documented and included in your report. The petitioner will be informed of any deficiencies in the method and asked to resolve them.

Please obtain the necessary analytical reference standards from the EPA Repository. If the analytical reference standard of fipronil and its metabolites are not available from the Repository, then please contact the Registration Specialist at RPA (Larry Hodges, 919-549-2870) directly requesting several hundred milligrams of each standard not available along with the required MSDS be provided directly to ACL to start the PMV. In your final report please note that all standards are or are not available from the Repository as of           (date)          . Also confirm the Repository ordering codes for fipronil and its metabolites.

The review is not in expedite status. The Registration Division Product Manager for fipronil is Rick Keigwin. He should be contacted directly concerning the priority for completion of the PMV.

Please address your written reports to: E.T. Haeberer, Acting Chief, Chemistry Branch I, Tolerance Support, Health Effects Division (7509C)

Attachment 1- Experimental Design for PMV  
Attachment 2- Proposed Enforcement Method, MRID# 437766-04.  
Attachment 3- ILV, MRID# 437766-05.

cc (with Attachment 1 only): R. Keigwin/A. Sibold (RD, 7505C), PP#5G04583, S.F.,  
Kramer, Circ., R.F., H. Hundley (ACB/BEAD-7503W), F. Griffith (PAM-II File),  
R. Griffin (RCAB-7509C)  
RDI: TPT1 (10/24/96), E.T. Haeberer (11/1/96). R.A. Loranger (10/31/96)  
G.F. Kramer:804V:CM#2:(703)305-5079:7509C:CBTS

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ATTACHMENT 1

METHOD: Fipronil- Validation of Method of Analysis for Fipronil and Its Metabolites in/on Potato and Cotton Matrices (Excluding Cotton Gin Trash). EC-95-303. MRID# 437766-04.

Please: (i) Indicate the limit of detection and quantitation; (ii) Do not use control values for recovery calculations; and (iii) Do not report control values as zero; if less than the limit of detection, report as such.

| RAC         | Chemicals Added | ppm Added | ppm Fipronil Found | % Rec. | ppm MB4595 Found | % Rec. | ppm MB46136 Found | % Rec. | ppm MB46513 Found | % Rec. | ppm RPA200766 Found | % Rec. |
|-------------|-----------------|-----------|--------------------|--------|------------------|--------|-------------------|--------|-------------------|--------|---------------------|--------|
| Cotton seed | Fipronil        | 0.000     |                    |        |                  |        |                   |        |                   |        |                     |        |
|             | MB 45950        | 0.005     |                    |        |                  |        |                   |        |                   |        |                     |        |
|             | MB 46136        | 0.010     |                    |        |                  |        |                   |        |                   |        |                     |        |
|             | MB 46513        |           |                    |        |                  |        |                   |        |                   |        |                     |        |
|             | RPA 200766      | 0.020     |                    |        |                  |        |                   |        |                   |        |                     |        |