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

MAY 7 1987

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

EXPEDITE

MEMORANDUM

SUBJECT: PP#'s 4F3074, 4F3007, and 4E3026. Propiconazole (Tilt® or CGA-64250) on Crops and Livestock Commodities. Additional Recovery Data, Sample Chromatograms, and Sample Calculation on Analytical Methods AG-454A and AG-517. Letter of April 6, 1987. MIRD No. 4014501. RCB No. 2174.

FROM: Sami Malak, Ph.D., Chemist
Tolerance Petition Section III
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

TO: Lois Rossi, PM #21
Fungicide-Herbicide Branch
Registration Division (TS-767)

THRU: Charles L. Trichilo, Ph.D., Chief
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

Note: This is an expedited review at the request of the Registration Division's Director, Mr. E. F. Tinsworth (Letter of 4/14/87).

Introduction and Background

In response to RCB memo of subject petitions (S. Malak, 3/13/87), Ciba-Geigy submitted additional recovery data, sample chromatograms, and sample calculation on analytical methods AG-454A and AG-517.

In the previously submitted methods the petitioner included validation studies for plant and animal commodities in which

recoveries were reported as averages. Accordingly, in our memo of 3/13/87, the petitioner was advised to submit the recoveries of the validation studies for small grains, rice, pecan nutmeats, bananas, eggs, milk, and meats of livestock as individual results, ranges, and averages. Furthermore, we requested submission of sample chromatograms of standard, fortified, and control samples, as well as sample calculations of the magnitude of residues in/on the above cited commodities.

Permanent tolerances are currently pending for residues of propiconazole (Tilt® or CGA-64250), 1-[[2(2,4-dicholrophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H1,2,4-triazole, in/on grains of wheat, barley, rye, and rice at 0.1 ppm; straw of wheat, barley, and rye at 1.5 ppm; rice straw at 3 ppm; kidney and liver of cattle, hogs, horses, sheep, and poultry at 0.1 ppm (PP#4F3074); pecans at 0.1 ppm (PP#4F3007); and bananas at 0.2 ppm (PP#4E3026).

A method trial has recently been completed in connection with PP#4F3074 for Ciba-Geigy's method AG-517, for the determination of propiconazole residues in livestock commodities and for Ciba-Geigy's method AG-454A for the determination of propiconazole residues in crops (memo of Everett Greer, et al, 4/27/87). Method AG-356 for crops and Method AG-359 for livestock commodities, previously submitted in connection with subject petitions, failed the method trial screen (P#4F3007, of R. Thomas, 9/9/86).

None of the above cited methods is capable of determining the free and conjugated compounds containing the triazole moiety contributed by propiconazole. The proposed enforcement method measures parent and metabolites as 2,4-dichlorobenzoic acid. Further, a deferral to TOX was made in connection with PP#4F3074 as to their concern regarding the toxicological significance of residues containing only the triazole moiety contributed by propiconazole in light of the fact that there are high background levels, presumably due to indigenous triazolealanine and other natural compounds containing the triazole moiety.

In this submission , the study title for the requested data is "Response to EPA's Request for Additional Recovery Information on Analytical Methods AG-454A and AG-517." The study is authored by M. W . Cheung of Ciba-Geigy, dated 4/3/87.

A. Recovery Data and Sample Chromatograms

1. Recovery Data of Propiconazole in Animal Tissues by AG-517:

In this study, cattle liver, round tissue, perirenal fat, eggs, and milk were fortified with propiconazole at various levels ranging from 0.02 to 0.1 ppm for milk and from 0.05 to 0.5 ppm for the remaining commodities. Individual recovery values, ranges and averages were reported in detail. Percent recoveries, reported as ranges (averages in parenthesis), were: liver 70-135 (96), round tissue 82127 (105), perirenal fat 64-128 (89), eggs 77-90 (84), and milk 63-87 (75). Adequate sample chomatograms of standard, fortified, and control samples are included.

2. Recovery Data of Propiconazole in Crops by AG-454A

Various commodities of wheat, soybeans, corn, celery, and legumes were fortified with propiconazole at levels ranging from 0.05 to 2.0 ppm. Individual recovery values, ranges, and averages were reported in detail. Percent recoveries, rported as ranges (averages in parenthesis), were: wheat 76-85 (80), soybeans 74-130 (92), corn 71135 (87), celery 68-117 (86), and legumes 74-133 (88). Adequate sample chomatograms of standard, fortified, and control samples are included.

B. Sample Calculation

Propiconazole recovery from a fortified crop sample was reported at 98%.

1. In 0.045 mg of crop sample, 0.004 ng of 2,4-dichlorobenzoic acid (DCBA) was found.

2. ppm DCBA equivalent = $\frac{0.004}{0.045}$ = 0.0888 ppm

3. ppm propiconazole equivalent = 0.0888 x 1.79[1/]

= 0.159 ppm.

4. Corrected for average recovery : $\frac{0.159}{0.98}$ = 0.16 ppm

RCB determined that all livestock residue data are invalid because of the failure of the method trial screen (memo of S. Malak and W. T. Chin, 3/20/87, subject petition). Whereas, residue data for crops using method AG-356 are valid, since the resolution of the GC/MS analyses of the

latter method (AG-356) is reasonably adequate. Ciba-Geigy has responded, under separate action, to the question regarding propiconazole residues in livestock commodities (see PP#4F3074 , MIRD No. 40150701, Letter of April 2, 1987). RCB will respond to this action under separate memo.

1/ A conversion factor based on the ratio of the molecular weight of DCBA 191.2 and propiconazole 342.22.

Conclusions

1. Adequate recovery data and sample chromatograms of standard, fortified, and control samples of livestock commodities using Ciba-Geigy's Method AG-517; and of crop commodities using Ciba-Geigy's Method AG-454A are available. Sample calculations are also included.

2. Ciba-Geigy has complied with data requirements requested in RCB's memo of subject petitions (S. malak, 3/13/87).

   This deficiency is resolved.

Recommendations

1. We recommend inclusion of these data as part of the method try out results of Ciba-Geigy's Methods AG-517 for livestocks and AG-454A for crops.

2. At this time, RCB continues to recommend against the requested tolerances in subject petitions for residues of propiconazole in or on crop and livestock commodities until the following deficiencies are resolved:

   a. Addressing the issue of the triazole moiety contributed by Tilt, currently pending in the Toxicology Branch, as to its toxicological significance and if there is a need for its inclusion in the tolerance expression. (PP#4F3074).

   b. Evaluation of the livestock residue data recently submitted by Ciba-Geigy in response to Malak/Chin memo of 3/20/87 (PP#4F3074).

c. Evaluation and reporting on the results of two method trials for Tilt, recently completed by the Analytical Chemistry Laboratory/COB/BUD in Beltsville. To allow the registrant's method to be used as an enforcement method, certain modifications are needed; these changes were relayed to Richard Conn of Ciba-Geigy by S. Malak on 4/29/87. A completed corrected copy of the enforcement method is needed for distribution to enforcement personnel.

d. Addressing deficiencies 4(a) and 4(b) in PP#4F3074 (memo of A. Smith, 4/9/85) regarding the need for residue data for the forage and hay of small grains, or submitting a revised Section B by imposing a grazing and feeding restriction for these commodities.

e. Addressing deficiency #5 stated in a memo by A. Smith, (PP#4F3074, 4/9/85) by proposing appropriate tolerances for livestock commodiies.

Note to PM

The petitioner should be advised to resolve deficiencies 2d, 2e, and submit method modifications as stated in deficiency 2c above under Recommendations.

cc: Circu, RF. SF (propiconazole or Tilt®), S. Malak, PP#4F3007, PP#4F3074, PP#4E3026, and PM # 21.

RDI: P. V. Errico:4/1/87:R. D. Schmitt:4/4/87
TS-769C:RCB:CM#2:RM814A:S.Malak:X557-4379:4/27/87