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

MAR 13 1991

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM

SUBJECT: PP#9F3743 - Clethodim (Select® in/on Soybean, Cottonseed, and Animal Commodities. Review of the December 19, 1990 Amendment (MRID No. 417307-01) [DEB No. 7552 and 7701] (HED Project No. 1-0460 and 1-0718)

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RSQ

Valent U.S.A. Corporation has submitted these amendments consisting of two cover letters and a supplementary Section D (revised confirmatory analytical method) in response to deficiencies outlined and summarized in our November 9, 1990, review by F.D. Griffith, Jr. The deficiencies are listed and repeated in the body of this review in the order they appeared in the review, followed by the petitioner's responses, then CBTS comments. Our conclusions and recommendations follow.

EXECUTIVE SUMMARY OF CHEMISTRY DEFICIENCIES

Run Petition Method Validations (PMV) on the proposed enforcement method and the confirmatory method.

Address product chemistry deficiencies.

CONCLUSIONS

1. Chemistry Branch (CB) Conclusion on **Residue Analytical Methods**

a. CBTS has requested ACB/BEAD to conduct a new PMV on the revised version of Analytical Method RM-26B-2 (MRID No. 416234-01), the proposed primary enforcement method (see memorandum by F.D. Griffith, Jr., to D.A. Marlow on October 23, 1990). CBTS defers judgment on the method being an enforcement method pending review of a new ACB/BEAD PMV report. The deficiency remains unresolved and continues outstanding.

b. The petitioner has submitted a quantity of the internal standard cloproxydim (reference grade) along with supporting documentation, i.e., the Material Safety Data Sheets (MSDS), to EPA's Pesticides and Industrial Chemicals Repository. Although some questions remain on the adequacy of the MSDS, CB will not consider this to be a deficiency at this time. The deficiency is resolved.

c. The petitioner has resubmitted the revised compound-specific confirmatory method further revised in accordance with our eight concerns as noted in the body of this review. The method is now suitable to initiate a PMV. This part of the deficiency is resolved.

d. CBTS has requested ACB/BEAD conduct a new PMV on the revised version of Analytical Method RM-26D-1 (MRID No. 417307-01), the proposed compound-specific confirmatory method (see memorandum by F.D. Griffith, Jr., to D.A. Marlow on February 20, 1991). CBTS defers judgment on the method being an enforcement procedure pending review of the ACB/BEAD PMV report. The deficiency remains unresolved and continues outstanding.

2. CB Conclusion on **Product Chemistry**

CB reiterates that the deficiencies associated with the product chemistry of clethodim will need to be resolved prior to the establishment of the proposed tolerances of this petition. These are discussed in CBTS's review of January 15, 1991. The deficiencies are listed in Table A, Generic Data Requirements for Clethodim Technical Grade, which see for details. The deficiency is not resolved and continues outstanding.

RECOMMENDATION

At this time, CB recommends against the establishment of the proposed clethodim plus its metabolites containing the 2-cyclohexen-1-one moiety tolerance in or on the commodities of this petition for reasons cited in our Executive Summary and further explained in Conclusions 1 and 2 above.

For further consideration of the proposed tolerances, the petitioner should be advised to resolve the deficiencies noted above.

DETAILED CONSIDERATIONS

RESIDUE ANALYTICAL METHODS

Deficiency

Petition Method Validation (PMV) on the primary enforcement method needs to be completed by ACB/BEAD.

Petitioner's Response

The petitioner is not required to respond.

CB Comments

CBTS reiterates that it has requested BEAD conduct a new PMV trial of the revised version (Analytical Method RM-26B-2; MRID No. 416234-01) of the proposed primary enforcement method ("comment moiety"). See memorandum by F.D. Griffith to D.A. Marlow dated October 23, 1990. CBTS defers further judgment on the adequacy of this method pending receipt/review of BEAD's PMV report. The deficiency remains unresolved and continues outstanding.

Deficiency

CBTS reiterates that the petitioner needs to submit a quantity of the internal standard cloproxydim (reference grade) along with supporting documentation, i.e., the Material Safety Data Sheet (MSDS), to EPA's Pesticides and Industrial Chemicals Repository. The deficiency remains unresolved and continues outstanding.

Petitioner's Response

In the cover letter, the petitioner claims to have submitted the cloproxydim sulfoxide standard to EPA's Repository in December 1990. A telcon (P. Beyer to D. Griffith on February 25, 1991) confirmed that a small quantity of this standard is at the Repository. However, there is some question as to the adequacy of the MSDS that could delay initial distribution of the standard. CB will not consider this to be a deficiency at this time. Since the standard is in the Repository, the deficiency is resolved.

Deficiency

The petitioner needs to resubmit the compound-specific confirmatory method further revised in accordance with our eight concerns as noted in the body of this review. This deficiency overall remains unresolved and continues outstanding.

Petitioner's Response (See MRID # 417307-01)

The petitioner has presented a further revised compound-specific confirmatory residue analytical method titled "Supplemental to: Confirmatory Method for the Determination of Clethodim and Clethodim Metabolites in Crops, Animal Tissues, Milk, and Eggs; RM-26D-1" by J.C. Lai, dated December 14, 1990.

CB Comments

Previously we considered method RM-26D-1 not sufficiently detailed to initiate a PMV. The method was remanded to the petitioner for further detailed write-up to include the following points. The petitioner needed to compare this method to the level of detail in RM-26B-2 and strive to have both methods at the same level of detail. Each point will be listed followed by our comments on his responses.

1. In Reagents, the use of the term "glass distilled" is not adequate to identify quality. The petitioner should spell out the solvent of choice, identify the manufacturer, and provide a catalogue number, then add "or equivalent." There needs to be more details on what $Ca(OH)_2$, NaCl, NaOH, and Celite were used. DEB questions the use of reagent grade Na_2SO_4 to be adequate for drying organic extracts. We suggest that the use of anhydrous Na_2SO_4, granular form, suitable for residue analysis be specified.

For solvents the petitioner has identified the solvent of choice, named the solvent manufacturer, and provided a catalogue number. The petitioner has identified the $Ca(OH)_2$ as Baker Analyzed® Reagent Powder, the NaCl as Baker Analyzed® Reagent Crystal, the NaOH as Baker Analyzed Reagent 50% Solution, and the Celite as Celite 545 Baker Analyzed Reagent. The Na_2SO_4 is now identified as anhydrous granular Baker Analyzed Reagent. Catalogue numbers were provided for all reagents and the petitioner allowed equivalent grade substitution. This part of the deficiency is resolved.

2. In Equipment, the source of all glassware needs to be specified. The size(s) of the Buchner funnels need to be clearly identified in each step. The model and manufacturer of the low-speed centrifuge, magnetic stir plates, reciprocating shaker, and rotary evaporator need to be identified followed by the phrase "or equivalent." The phrase "or equivalent" should be added after the description

of the LC. For the silica Sep Paks, the petitioner needs to provide a catalogue number.

Glassware sources are identified by catalogue name and number. The Buchner funnels are Coors 6024 series, 126 mm diameter for the extraction step and alkaline precipitation step. The low-speed centrifuge is a Beckman, Model GPKR. The magnetic stir plates are Corning, Model PC-351. The reciprocating shaker is Eberbach, Model 6010. The rotary evaporator is a Buchi, Model ROT-M, with a water bath. The petitioner allows for equipment substitution by inserting the phrase "or equivalent" after each piece of equipment. The silica Sep-Pak® are Waters Associates # 51900. This part of the deficiency is resolved.

3. In the Extraction, the size of the Buchner funnel needs to be identified.

The size of the Buchner funnel is 126 mm diameter for both the extraction step and the alkaline precipitation step. This part of the deficiency is resolved.

4. In the Alkaline Precipitation, DEB points out this is an alkaline solution to which 5 mL of concentrated HCl are added and "mix well." DEB feels this step needs additional detail on mixing, heat evolution, gas, etc.

The petitioner's directions are now to carefully add 5 mL conc. HCl and mix well with adequate venting. The petitioner points out possible heat and gas formation. This part of the deficiency is resolved.

5. In the Liquid-Liquid Partitioning step, the addition of internal standard should be moved to the extraction step. The IS should be added when the recovery standards are added. The size or amount of Na_2SO_4 in the bed needs to be identified. A "room temperature" water bath is insufficient detail. The petitioner needs to identify a preferred temperature; e.g., 25 °C.

The petitioner has removed the addition of cloproxydim sulfoxide from the liquid-liquid partitioning step and it is now included in the extraction step. The amount of anh. Na_2SO_4 is 150 grams in a 10 cm filter funnel. The water bath temperature is 20 to 25 °C. This part of the deficiency is resolved.

6. In the Oxidation step, the reaction is to proceed "exactly 15 minutes." The petitioner needs to document why exactly 15, not 12 or 20, minutes is necessary. The consequences of using either a shorter or longer oxidization time need to be fully documented.

The petitioner now states the reaction is to proceed "for approximately 15 minutes." This is an acceptable direction. This part of the deficiency is resolved.

7. In the Silica Sep Pak, the petitioner needs to define the method of elution from the Sep Pak®, i.e., gravity flow, syringe push, or vacuum pull.

The elutions through the Sep Paks® are all gravity flow. This part of the deficiency is resolved.

8. In the Animal Tissue Extraction step, the size Buchner funnel used and the amount of celite (what kind?) need to be clearly identified.

The funnel size is 126 mm and the amount of celite is 25 grams of Celite 545. This part of the deficiency is resolved.

CB notes the petitioner has included the justification for use of diazomethane as the methylating agent in an appendix to this procedure. CBTS has previously accepted this justification. We note other methylating agents were not as efficient.

If the petitioner agrees, CBTS proposes deleting the word "approximately" from both extraction steps. The extraction step will then read "Weigh 50 grams . . . ." This makes the method an external standard calculation method, and the addition of cloproxydim sulfoxide will serve as an optional marker compound in addition to being an internal standard. The method in its present format is an internal standard procedure. With the small amount of cloproxydim sulfoxide available, the confirmatory procedure needs to be an external standard calculation method. However, if the petitioner objects to CB's proposed change to the procedure, then the PMV initiated on February 20, 1991 will have to be terminated, the method remanded to the petitioner to be rewritten as an external standard procedure, be resubmitted and reviewed again before a new PMV can be initiated.

CBTS assumes the petitioner agrees to delete the word "approximately" in the initial weighing step. Thus we conclude the method is suitable for a PMV. The petitioner has resubmitted the requested revised compound-specific confirmatory method further revised in accordance with our eight concerns as noted above. This part of the deficiency is resolved.

In response to concerns noted in Valent's February 14, 1991 letter (signed by Patricia B. Pomidor, Product Manager), we point out that second lab validation is no proof the method will work. It assures us of a better write-up and a better chance the method will successfully complete a PMV on the first attempt. After careful consideration, CB concludes a PMV is necessary for the compound-specific confirmatory method. The primary enforcement

method will be common moiety method. However, before any regulatory action is initiated on any sample, the identity and levels of clethodim and/or its metabolites will need to be confirmed by the compound-specific method.

CBTS has requested ACB/BEAD conduct a new PMV on the revised version of the Analytical Method RM-26D-1 (MRID No. 417307-01), the proposed compound-specific confirmatory method (see memorandum by F.D. Griffith, Jr., to D.A. Marlow on February 20, 1991). CBTS defers judgment on the method being an enforcement procedure pending review of the ACB/BEAD PMV report. The deficiency remains unresolved and continues outstanding.

PRODUCT CHEMISTRY

Deficiency

The deficiencies associated with the product chemistry of clethodim will need to be resolved prior to the establishment of the proposed tolerances of this petition. These are discussed in the CBTS review of January 15, 1991, by F.D. Griffith, Jr. The deficiencies are listed in Table 1A, Generic Data Requirements for Clethodim, Technical Grade, which see, for details.

Petitioner's Response

The petitioner has not responded.

CB Comments

CB reiterates the deficiency. It continues unresolved and remains outstanding.

H7509C:CBTS:Reviewer(FDG):CM#2:Rm814B:557-0826:JOB:62832:I:WP5.0:
C.Disk:KEVRIC:03/06/91:CL:WO:CL:WO:DD:ed:fdg:3/11/91.

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RDI:SecHd:RSQuick:3/12/91:BrSrSci:RALoranger:3/12/91.