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

NOV 19 1990

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#9F3743 - Clethodim (Select®) in/on Soybeans, Cottonseed, and Animal Commodities. Review of September 5, 1990 Amendment. (MRID No. 416234-01, -02, -03, -04, and -05) [DEB No. 7062] (HED Project No. 0-1940)

FROM: Francis D. Griffith, Jr., Chemist
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TO: Joanne I. Miller, Acting PM 23
Fungicide-Herbicide Branch
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and

Toxicology Branch - Fungicide, Herbicide Support
Health Effects Division (H7509C)

THRU: Richard D. Schmitt, Ph.D., Chief
Chemistry Branch I - Tolerance Support
Health Effects Division (H7509C)

Valent U.S.A. Corporation has submitted this amendment consisting of a cover letter, a supplementary Section D (revised analytical method and storage stability data), and a revised Section F (new tolerance proposal) in response to deficiencies outlined and summarized in our reviews of March 12, May 4, and June 20, 1990 all by M.J. Nelson. The deficiencies are listed and repeated in the body of this review in the order they appeared in those reviews followed by the petitioner's responses, then DEB comments. Our conclusions and recommendations follow.

EXECUTIVE SUMMARY OF CHEMISTRY DEFICIENCIES

- Run a Petition Method Validation (PMV) on the proposed enforcement method and the confirmatory method.

- Submit a quantity of the internal standard (cloproxydim sulfoxide) to the Pesticides and Industrial Chemicals Repository, Research Triangle Park, NC.

- Resubmit the compound-specific confirmatory procedure, revised in accordance with our suggestions and provide second laboratory validation for the procedure.

- Address Product Chemistry deficiencies.

CONCLUSIONS

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

   a. The petitioner has presented a rewritten residue analytical enforcement method (RM-26B-2) that addresses all points noted in our previous reviews. The method is now suitable to initiate a PMV. The deficiency is resolved.

   b. 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 F.D. Griffith, Jr. to D.A. Marlow, 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.

   c. 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 Sheets, to EPA's Pesticides and Industrial Chemicals Repository. The deficiency remains unresolved and continues outstanding.

   d. 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 over all remains outstanding and continues outstanding.

      As for the concerns expressed in CB's May 4, 1990 review on the confirmatory method, the petitioner still needs to provide independent laboratory validation data for the method and also to explain why diazomethane is needed as the methylating agent in the method.

2. CB Conclusion on **Storage Stability**

a. The petitioner has presented results of a storage stability study using field-incurred residues in soybean hulls, soybean meal, and soybean crude oil and soapstock. This part of the deficiency is resolved.

b. The petitioner has presented results of a storage stability study using field-incurred residues in cottonseed hulls, cottonseed meal, cottonseed crude oil, and soapstock. This part of the deficiency is resolved.

c. CB concludes that total clethodim residues are stable in cattle tissues (liver, kidney, fat, muscle) and milk in frozen storage (-20 °C). These deficiencies are resolved.

d. CB concludes that total clethodim residue are stable in poultry tissue (liver, gizzard, fat, muscle) and eggs stored frozen (-20 °C). The deficiency is resolved.

e. CB concludes that total clethodim residues are stable in soybean seed macerates and fuzzy cottonseed macerates stored frozen (-20 °C). These deficiencies are resolved.

3. CB Conclusion on **Magnitude of the Residue - Crop Field Trials**

The residue analytical method is satisfactory to gather residue data and the petitioner has provided an adequate amount of geographically representative crop field trial data on soybeans and soybeans. Residues of total clethodim are not expected to exceed the proposed 1 ppm and 10 ppm tolerances on cottonseed and soybeans respectively under the proposed conditions of use for Select® Herbicide. The deficiency is resolved.

4. CB Conclusion on **Magnitude of the Residue - Processed Foods/Feeds**

a. CB concludes an adequate conventional soybean processing study has been conducted depicting concentration (or decline) of total clethodim residues in soybean hulls, meal, crude and refined oil, and soapstock from soybeans bearing detectable residues. Concentration of residue was shown in soybean soapstock (1.25X) and the petitioner has proposed a 15 ppm tolerance for total clethodim in soybean soapstock. The deficiency is resolved.

b. CB also concludes an adequate conventional cottonseed processing study has been conducted depicting concentration (or decline) of total clethodim residues

in cottonseed hulls, meal, crude oil, refined oil, and soapstock from undelinted cottonseed bearing detectable residues. Concentration of residue was observed in cottonseed meal (1.69X) and the petitioner has proposed a 2 ppm tolerance for total clethodim residues in cottonseed meal. The deficiency is resolved.

5. CB Conclusion on **Proposed Tolerance**

Judgment on the adequacy of these tolerances is deferred until there have been successful PMVs. CB tentatively concludes that residues of total clethodim are not expected to exceed the proposed tolerances from the proposed conditions of use of Select® Herbicide.

6. 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 DEB's companion reviews titled "PP#9F3743. Clethodim Product Chemistry Data Submitted in Support of Registration," M. Nelson, DEB No. 5681, dated March 12, 1990, 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, 5, and 6 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 (From our June 20,1990 review)

"By memorandum dated April 16, 1990, DEB (M. Nelson) requested ACB/BEAD conduct a PMV trial of Valent/Chevron Analytical Method RM-26B-1 titled "The Determination of Clethodim Residues in Crops, Chicken and Beet Tissues, Milk, and Eggs.

"ACB/BEAD (E. Greer) has responded by memorandum dated June 14, 1990 that their pretrial review of this method indicates

difficulties (enumerated in their memorandum) would be encountered by an analyst if this PMV trial were to be attempted on the method in its present form. ACB/BEAD suggests Method RM-26B-1 be rewritten so as to address the deficiencies noted in their memorandum.

"A copy of ACB/BEAD's memorandum of June 14, 1990 is attached to this review. The PM should send a copy of it in its entirety to the petitioner with the request that Analytical Method RM-26B-1 be revised to appropriately address the concerns raised by ACB/BEAD."

Petitioner's Response (See MRID No. 416234-01)

In response to the ACB/BEAD memorandum by E. Greer of June 14, 1990, the petitioner has presented a revised analytical residue method titled "The Determination of Clethodim Residues in Crops, Chicken and Beef Tissues, Milk, and Eggs Method: RM-26B-2" by B. Ho, dated August 15, 1990, 17 pages.

DEB Comments

In the preparation of the $Ba(OH)_2$ solution, the petitioner suggests to gravity filter the solution through a 10 cm filter funnel lined with Whitman 2V into a 100 mL graduated cylinder.

After sampling soapstock and dry feeds, the instructions are for the analyst to proceed to the extraction step. Extracts are to be evaporated by rotary evaporator in a 30 °C water bath.

In the precipitation step, the petitioner now uses a 1 liter round bottom flask. For partitioning, a 1 liter separatory funnel is used. After shaking and allowing phases to separate then the 4 x 100 organic phases are collected in a 1 liter round bottom flask before being rotary evaporated to dryness.

In the oxidation step, the 10 mL of 30% H_2O_2 is added through the Bantam-Ware separatory funnel. On removal of excess H_2O_2, the sample extract is evaporated to dryness using a rotary evaporator. After methylation, the solution is evaporated using a rotary evaporator.

The criteria for determining if additional cleanup is necessary is that if initial GC analysis shows the limit of detection cannot be reached and matrix coextractive peaks or unidentified analytical responses (UARs) interfere, then another aliquot of sample is reextracted and a silica gel cleanup is used after methylation. The second cleanup step is used only after GC analysis following silica gel cleanup still shows positive interference. After methylation and a gas chromatography (GC) analysis showing positive interference then the sample is evaporated to dryness using a rotary evaporator. If the initial cleanup showed interference, then the sample is put into a 50 mL round bottom flask for rotary evaporation prior to the silica gel cleanup. Going from the silica gel cleanup to the C18 cartridge

cleanup, the extracts are taken to dryness using a 50 mL round bottom flask for rotary evaporation.

For C18 cartridge cleanup, elution is by gravity feed and the 2 x 5 mL 30% CH_3OH/70% H_2O eluate is collected in a small beaker. The eluate is transferred to a 125 mL separatory funnel then partitioned 3 x 10 mL EtOAc.

The formula for concentration calculations now reads

$$\underline{ug}/mL = \left(\frac{area}{A}\right)^{1/B}$$

The deficiencies in method writeup as noted in the ACB/BEAD memorandum by E. Greer on June 14, 1990 have been addressed by the petitioner. This part of the deficiency is resolved.

The petitioner's proposed enforcement method involves a 100 mL water and/or a 300 mL CH_2OH extraction of 5 grams (for soapstock) to 50 grams (for milk and eggs) in a blender for 5 minutes. After concentration via rotary evaporation, the first cleanup step involves alkaline precipitation with $Ca(OH)_2$ in 1 gram per 10 grams of sample. The extracts are acidified with 5 mL conc. HCl then back-extracted/partitioned with 4 x 100 mL CH_2Cl_2. Clethodim and its metabolites are oxidized to a dicarboxylic acid in 100 mL of 1% $Ba(OH)_2$ then while reflux is going 20 mL of 30% H_2O_2 is added through the Bantam-Ware separatory funnel attached to the reflux column side arm.

The oxidized solution is cooled to room temperature and the pH is adjusted to 7 followed by addition of catalase. Potassium pyrosulfite is added until pH is 4.0 to 4.5 and all oxidant is gone. The extract is methylated to form the dimethyl ester by use of 90 mL anhydrous CH_3OH and a 30-minute reflux. The solution is cooled and pH is adjusted with $NaHCO_3$ until pH $\geq$ 7. The dimethyl esters are partitioned out with 2 x 100 mL CH_2Cl_2, solvent exchanged to acetone, then rotary evaporated to 2.0 mL for GC analysis.

If initial GC analysis shows either UARs that interfere, or the limit of detection cannot be obtained, then 1 or 2 alternate cleanup steps using first a silica cleanup column and if sample still shows UARs then a C18 Sep Pak® cartridge is used. Another aliquot of sample is extract3ed if additional cleanup is required.

Determination is by GC using a Hewlett-Packard, Model 5890 GC equipped with a flame photometric detector (FPD) operated in the sulfur mode. The GC column is a 0.53 mm (id) x 10 m fused silica capillary coated with HP-1 or HP-17. Temperature parameters for a isothermal run and two programmed temperature runs were provided. Quantification is by peak area and amount is read from a standard curve.

This method, RM-26B-2, is suitable to gather residue data.

Deficiency (From our May 4, 1990 review)

Run Method Validation Trial(s) by ACB/BEAD.

Petitioner's Response

The petitioner is not required to respond.

CB Comments

DEB 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 ("common moiety"). See memorandum by F.D. Griffith to D.A. Marlow dated October 23, 1990. DEB 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 (From our May 4, 1990 review)

Submit a quantity of the internal standard (cloproxydim sulfoxide) to the Pesticides and Industrial Chemicals Repository, Research Triangle Park, NC.

Petitioner's Response

The petitioner did not respond.

DEB Comments

In a telecon on October 16, 1990 from D. Griffith, EPA/CBTS to P. Beyer, EPA Repository, we learned the internal standard cloproxydim sulfoxide is not at the Repository.

The petitioner has been informed that this standard is still not at EPA's Pesticides and Industrial Chemicals Repository (telecon D. Griffith, EPA, to P. Pamidor, Valent, on October 16, 1990). The petitioner agreed to supply the standard to our Repository and a 100 mg portion to EPA's Analytical Chemistry Laboratory in Beltsville.

CBTS reiterates that a quantity of the internal standard, cloproxydim sulfoxide (reference grade), along with appropriate supporting documentation, should be submitted to the U.S. EPA Pesticides and Industrial Chemicals Repository, U.S. EPA Environmental Research Center, Research Triangle Park, NC 27711.

The deficiency is not resolved and continues outstanding.

Deficiency (From our May 4, 1990 review)

Resubmit the compound-specific Confirmatory Procedure, revised in accordance with our requests (including an interference study and independent laboratory validation).

The "compound-specific" confirmatory procedure, RM-26C-1, is not adequate, as written. Various revisions, additions, an interference study, and an independent laboratory validation study are required.

Petitioner's Response (See MRID No. 416234-02)

The petitioner has presented a revised confirmatory method titled "Confirmatory Method for the Determination of Clethodim and Clethodim Metabolites in Crops, Animal Tissues, Milk, and Eggs" by B. Ho, dated August 23, 1990 and coded Laboratory Project Identification RM-26D-1.

DEB Comments

In our May 4, 1990 amendment review by M.J. Nelson, DEB detailed six areas of concern for a revised method.

The title of the method now includes "Determination of Clethodim and Clethodim Metabolites . . . ." This part of the deficiency is resolved.

The petitioner continues to propose methylation via diazomethane CH_3N_2. CB suggests that Attachment IV to the September 5, 1990 cover letter be incorporated into the method writeup. The attachment has not been forwarded to CB for review, thus we are unable to comment on the petitioner's arguments why CH_2N_2 is the methylating agent of choice. This part of the deficiency continues unresolved and remains outstanding.

The analytical residue method has been modified and expanded to include applicability to animal tissues (meat and poultry), milk, and eggs. The title and writeup have been revised. This part of the deficiency is resolved.

The petitioner has provided clethodim sulfoxide recovery data for fortifications of 0.02 to 0.2 ppm in beef liver, beef muscle, milk, and eggs. Clethodim sulfoxide recoveries in beef liver and muscle ranged from 87 to 119 percent (n = 18). Clethodim sulfoxide recoveries from eggs spiked at 0.05 and 0.2 ppm ranged from 94 to 124 percent (n = 9). For clethodim sulfoxide fortified in milk at 0.02 and 0.05 ppm, recoveries ranged from 84 to 123 percent (n = 9). The petitioner provided copies of HPLC chromatograms showing standards of clethodim sulfoxide and the internal standards(IS); untreated controls of beef muscle, beef liver, milk, and eggs. Chromatograms showing clethodim sulfoxide at 0.05 and 0.2 ppm in beef liver and beef muscle; clethodim sulfoxide in milk at 0.02 and 0.05 ppm; and clethodim sulfoxide in eggs at 0.05 and 0.2 ppm were presented. For beef liver and beef muscle, CB notes a number of UARs are

present in chromatograms at the limit of detection. We estimate the clethodim sulfoxide equivalents in these matrices at 0.01 to 0.02 ppm. Chromatograms of milk and egg extracts were freer of UARs and a LD of 0.01 to 0.02 ppm is appropriate. UARs were not present in the IS or clethodim sulfoxide retention windows. The petitioner has provided adequate supporting HPLC chromatographic data. This part of the deficiency is resolved.

The petitioner has presented the results of an interference study run in the matrices of beef liver, milk, and soybeans to show HPLC separation of sethoxydim, sethoxydim sulfoxide, and 5-OH sethoxydim sulfoxide from clethodim, clethodim sulfoxide, and 5-OH clethodim sulfoxide alone and in combination. The IS cloproxydim sulfoxide was included in all chromatograms. In beef liver fortified at 0.2 ppm clethodim sulfoxide plus 0.2 ppm sethoxydim sulfoxide, clethodim sulfoxide recoveries alone were 97 percent, and sethoxydim recoveries alone were 74 to 104 percent. Clethodim sulfoxide plus sethoxydim together can be completely separated in beef liver with clethodim sulfoxide recoveries of 127/130 percent and sethoxydim recoveries of 92/100 percent. Similar situations for milk gave comparable excellent recoveries. At 0.05 ppm clethodim sulfoxide plus 0.05 ppm sethoxydim sulfoxide in milk separation was complete and recoveries were above 100 percent.

Soybean seed was spiked with 5 ppm of 5-OH clethodim sulfoxide plus clethodim sulfoxide, 5 ppm sethoxydim sulfoxide, and 5 ppm 5-OH sethoxydim sulfoxide alone and in combination. 5-OH clethodim sulfoxide recoveries ranged from 81 to 96 percent whether alone or with sethoxydim metabolites. Clethodim sulfoxide recoveries ranged from 89 to 96 percent whether alone or with sethoxydim metabolites. Sethoxydim sulfoxide had adequate recovery whether spiked alone (110%) or in combination with clethodim metabolites (106/109%). 5-OH sethoxydim sulfoxide through the confirmatory clethodim procedure had low recoveries of 30 to 45 percent. In all cases, clethodim metabolites could easily be separated from sethoxydim metabolites. This is confirmed by review of supporting HPLC chromatographic data. The petitioner has provided copies of HPLC chromatograms to verify the data generated. DEB agreed with the proposed HPLC conditions to separate clethodim plus its metabolites from sethoxydim plus its metabolites. UARs were minimal at the 5 ppm level used in this interference study. The petitioner has conducted the requested interference study to show that sethoxydim metabolites can be completely separated from clethodim and its metabolites. This part of the deficiency is resolved.

DEB also requested independent laboratory validation data for the clethodim confirmatory method. None has been yet provided. Thus, DEB reiterates the deficiency.

In summary, the compound specific confirmatory method has 50 grams of plant material extracted with 150 to 200 mL of CH_3OH/H_2O (80/20 v/v) 5 minutes on an Omni mixer. The extract is filtered. Alkaline precipitation cleanup using 2 grams $Ca(OH)_2$ is the next

step. The solution is acidified and partitioned 3 x 100 mL CH_2Cl_2 from a NaCl solution. The CH_2Cl_2 is dried over Na_2SO_4 then methylated with CH_2N_2. The dimethyl esters are base washed with 0.1 N NaOH, then oxidized with 250 mg of m-chloroperbenzoic acid with excess oxidizing agent removed after 15 minutes with 2 percent (w/v) sodium thiosulfate. Further cleanup is on Sep Pak®. Analysis is by HPLC using a Hypersil ODS 3 um 15 cm x 4.6 mm column (Shandon) at 1.0 mL/min flow gradient elution of water and ACN for a 45-minute total run time. Injected volume is 20 uL. The determination is UV at 270 nm with 254 nm as the alternate wavelength.

For animal tissues, eggs, or milk, the procedure is almost identical using a CH_3OH extraction, alkaline precipitation, acidification, CH_2Cl_2 partitioning, CH_2N_2 methylation, followed by oxidization with m-chloroperbenzoic acid and HPLC UV determination using gradient elution H_2O and ACN with a Hypersil ODS, 15 cm x 4.6 mm column and the UV detector set at 254 nm.

DEB concludes the confirmatory method is suitable to gather residue data. The method is significantly different from the enforcement procedure now undergoing a PMV. This procedure also needs a PMV. This is a deficiency.

Previously in DEB's May 4, 1990 memorandum, we requested the petitioner scrutinize the level of detail of the confirmatory method to have it at the same level as the proposed enforcement procedure. We do not consider method RM-26D-1 sufficiently detailed to initiate a PMV. The method is remanded to the petitioner for further detailed writeup to include the following points. The petitioner needs 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.

1. In Reagents, the use of 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.

2. In Equipment, the source of all glassware needs to be specified. The size(s) of the Buchner funnels needs 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.

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

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

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.

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.

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, vacuum pull.

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

When the petitioner has prepared a rewritten/corrected version of method RM-26D-1, a PMV will be considered. This is a deficiency.

STORAGE STABILITY

Deficiency

Submit freezer storage stability studies for soybean processing fractions and cottonseed processing fractions.

From our March 12, 1990 review:

9. DEB concludes the petitioner must demonstrate via a freezer storage stability study that total clethodim residues (DME + DME-OH) are stable in soybean processing fractions (as listed in Table F) stored frozen (-20 °C) for up to 3 1/2 months.

11. DEB concludes the petitioner must demonstrate via a freezer storage stability study that total clethodim residues (DME + DME-OH) are stable in cottonseed processing fractions (as listed in Table G) stored frozen (-20 °C) for up to 2 months.

Petitioner's Response (See MRID Nos. 416234-03 and -04)

The petitioner has submitted the results of a clethodim storage stability study in soybean processing fractions titled "Freezer Storage Stability of Clethodim Residues on Soybean Processed Parts" by B. Ho dated July 27, 1990 and coded Laboratory Project ID T-6921SS.

The petitioner has submitted the results of a clethodim storage stability study in cottonseed processed fractions titled "Freezer Storage Stability of Clethodim Residues on Cottonseed Processed Parts" by B. Ho dated July 27, 1990 and coded Laboratory Project ID T-6912SS.

CB Comments

The petitioner conducted a storage stability study for clethodim residues in soybean processed fractions. The clethodim metabolite residues are the result of field-incurred residues from the field trial that was used in a soybean processing study. These magnitude of the clethodim residues on soybeans in trial T-6921, Iowa, 1987, and the processing study have been previously reviewed.

For this storage stability study, the initial clethodim analysis using method RM-26A-1 (the later rewritten version reviewed above and found to be satisfactory to gather residue data) serves as the time 0 (T = 0) value. These soybean processed fractions were stored at -20 °C in Zip-Loc bags and aliquots were removed at various time intervals for reanalysis. The soybean processed fractions used were hulls, meal, crude oil, soapstock, and crude lecithin.

Total clethodim residues (DME + DME-OH) in soybean hulls at T = 0 are 26.42 ppm. Reanalysis of soybean hulls at 75 days (2.5 months), 179 days (6 months), and 395 days (13.2 months) showed total clethodim residues ranged from 74 to 98 percent of the initial T = 0 value.

Total clethodim residues (DME + DME-OH) in soybean meal at T = 0, are 27.2 ppm. Reanalysis of soybean meal at 129, 156, and 260 days (8.7 months) showed total clethodim residues ranged from 96 to 131 percent of the initial T = 0 value.

Total clethodim residues (DME + DME-OH) in soybean crude oil at T = 0 are 2.77 ppm. Reanalysis of crude soybean oil at 126 and 224 days (7.5 months) showed total clethodim residues ranged from 85 to 103 percent of the initial T = 0 value.

Total clethodim residues (DME + DME-OH) in soybean soapstock at T = 0 are 33.38 ppm. Reanalysis of soybean soapstock at 252 days and 379 days showed total clethodim residues declined to 67 to 70 percent of the initial value.

These data show that total clethodim residues are stable in frozen storage of soybean processed fractions for at least 13 months. This part of the deficiency is resolved, i.e., deficiency 9 of our March 12, 1990 review.

The petitioner conducted a storage stability study for clethodim residues in cottonseed processed fractions. The clethodim metabolite residues are the results of field-incurred residues from the field trial that was used in a cottonseed processing study. These magnitude of the clethodim residues in cottonseed in Trial T-6912, Mississippi, 1987 and the processing study have been previously reviewed.

For this storage stability study, the initial clethodim analysis using method RM-26A-1 (the later rewritten version reviewed above and found satisfactory to gather residue data) serves as the time 0 (T = 0) value. These cottonseed processed fractions were stored at -20 °C in Zip-Loc bags and aliquots were removed at various time intervals for reanalysis. The cottonseed processed fractions used were cottonseed hulls, meal, crude oil, and soapstock.

Total clethodim residues (DME + DME-OH) in cottonseed hulls at T = 0 are 0.78 ppm. Reanalysis at 62 and 158 days (5.3 months) showed total clethodim residues ranged from 86 to 117 percent of the initial T = 0 value.

Total clethodim residues (DME + DME-OH) in cottonseed meal at T = 0 are 1.35 ppm. Reanalysis at the same time intervals as cottonseed hulls showed total clethodim residues ranged from 103 to 124 percent of the initial T = 0 value.

Total clethodim residues (DME + DME-OH) in cottonseed crude oil at T = 0 are 0.14 ppm. Reanalysis at 126, 224, 307, and 434 days (14.5 months) showed total clethodim residues ranged from 79 to 114 percent of the initial T = 0 value.

Total clethodim residues (DME + DME-OH) in cottonseed soapstock at T = 0 are 0.65 ppm. Reanalysis of cottonseed soapstock at 292 and 440 days (14.7 months) showed total clethodim residues ranged from 86 to 109 percent of the initial T = 0, value.

These data show that total clethodim residues are stable in storage of cottonseed processed fractions for at least 15 months. This part of the deficiency is resolved, i.e., Deficiency 11 of the March 12, 1990 review.

Deficiency (From our May 4, 1990 review)

Contingent upon the satisfactory resolution of analytical methods issues, DEB concludes that total clethodim residues are stable in cattle tissues (liver, kidney, fat, muscle) and milk stored frozen (-20 °C) for up to 5 months.

Subject to the favorable removal of this contingency, DEB can also consider Conclusions 12 and 18 of its March 12, 1990 review to be resolved.

CB Comments

Since CB concludes the residue analytical method is satisfactory to gather residue data, this contingency is removed. Deficiency 5 of our May 4, 1990 review and Deficiencies 12 and 18 of our March 12, 1990 review are all resolved.

CB concludes that total clethodim residues are stable in cattle tissues (liver, kidney, fat, muscle) and milk stored at -20 °C for at least 5 months.

Deficiency (From our May 4, 1990 review)

Contingent upon the satisfactory resolution of analytical methods issues, DEB concludes that total clethodim residues are stable in poultry tissues (liver, gizzard, fat, muscle) and eggs stored frozen (-20 °C) for up to 2 months.

Subject to the favorable removal of this contingency, DEB can also consider Conclusion 13 of its March 12, 1990 review of this petition to be resolved; re: Conclusion 19, a revised Section F remains outstanding.

CB Comments

Since CB concludes the residue analytical method is satisfactory to gather residue data, this contingency is removed. Deficiency 6 of our May 4, 1990 review and Deficiency 13 of our March 12, 1990 review are resolved.

CB concludes that total clethodim residues are stable in poultry tissues (liver, gizzard, fat, muscle) and eggs stored at -20 °C for at least 2 months.

Deficiency (From our March 12, 1990 review)

8. Contingent upon the satisfactory resolution of analytical methods issues, DEB concludes that total clethodim residues are stable in soybean seed macerates stored frozen (-20 °C) for up to 6 1/2 months.

10. Contingent upon the satisfactory resolution of analytical methods issues, DEB concludes that total clethodim residues are stable in fuzzy cottonseed macerates stored frozen (-20 °C) for up to 6 months.

CB Comments

Since CB concludes the residue analytical method is satisfactory to gather residue data, these contingencies are removed. Deficiencies 8 and 10 of our March 12, 1990 review are resolved.

CB concludes that total clethodim residues are stable in soybean seed macerates and fuzzy cottonseed macerates stored frozen (-20 °C) for at least 6 1/2 and 6 months, respectively.

MAGNITUDE OF THE RESIDUE - CROP FIELD TRIALS

Deficiency (From our March 12,1990 review)

14. Contingent upon the satisfactory resolution of analytical methods issues, DEB concludes the field trial data on soybeans provide adequate geographical representation and are sufficient to support the requested tolerance of 10.0 ppm in conjunction with the proposed use.

16. Contingent upon the satisfactory resolution of analytical methods issues, DEB concludes the field trial data on cotton provide adequate geographical representation. However, the requested tolerance of 5.0 ppm is too high in conjunction with the proposed use. A tolerance level of 1.0 ppm for cottonseed would be more appropriate, and should be proposed via a revised Section F.

CB Comments

Since CB concludes the residue analytical method is satisfactory to gather residue data, these contingencies are removed. Deficiencies 14 and 16 of our March 12, 1990 review are resolved.

CB concludes the field trial data on soybeans provide adequate geographical representation and are sufficient to support the requested tolerance of 10 ppm from the proposed use of Select® Herbicide.

CB concludes the field trial data on cotton provide adequate geographical representation and are sufficient to support the requested tolerance of 1 ppm from the proposed use of Select® Herbicide.

MAGNITUDE OF RESIDUE - PROCESSED FOODS/FEEDS

Deficiency (From our March 12,1990 review)

15. Contingent upon the satisfactory resolution of freezer storage stability and analytical methods issues, DEB concludes the processing trial data on soybeans are adequate, and that a revised Section F needs to be submitted to include a food additive tolerance proposal of 15 ppm for soybean soapstock in conjunction with the proposed tolerance level of 10.0 ppm on soybeans.

16. Contingent upon the satisfactory resolution of freezer storage stability and analytical methods issues, DEB concludes the processing trial data on cottonseed are adequate, and that a revised Section F needs to be submitted to include a food additive tolerance proposal of 2.0 ppm for cottonseed meal in conjunction with a revised tolerance proposal of 1.0 ppm on cottonseed.

CB Comments

Since CB concludes the residue analytical method is suitable to gather residue data and that adequate storage stability data have been presented for cottonseed processed fractions and soybean processed fractions, these contingencies are removed. Deficiencies 15 and 17 of our March 12, 1990 review are resolved.

CB concludes the petitioner has conducted a conventional soybean processing study depicting concentrations (or decline) of total clethodim residues in soybean hulls meal, crude oil, refined oil, and soybean soapstock from soybeans bearing detected residues. Concentration of residue was noted in soybean soapstock (1.25X). The petitioner has proposed a 15 ppm tolerance of total clethodim in soybean soapstock.

CB concludes the petitioner has conducted a conventional cottonseed processing study depicting concentration (or decline) of total residues in cottonseed hulls, meal, crude oil, refined oil, and soapstock from undelinted cottonseed bearing detected residues. Concentration of residue was observed in cottonseed meal (1.69X). The petitioner has proposed a 2 ppm tolerance of total clethodim in cottonseed meal.

PROPOSED TOLERANCE

Deficiency (From our May 4,1990 review)

Submit a revised Section F incorporating the following changes: soybean soapstock at 15 ppm; cottonseed at 1.0 ppm; cottonseed meal at 2.0 ppm; and eggs at 0.2 ppm.

Petitioner's Response

The petitioner has presented the following revised Section F:

1. Valent U.S.A. Corporation proposes that 40 CFR 180.101 be amended to establish a tolerance for the combined residues of the herbicide (E)-2-[1(((3-chloro-2-propenyl)oxy)iminopropyl]-5-[2-ethylthio)-propyl]-3-hydroxy-2-cyclohexene-1-one and its metabolites containing the 2-cyclohexene-1-one moiety (calculated as the herbicide) in or on the following raw agricultural commodities: soybeans at 10.0 ppm; cottonseed at 1.0 ppm; meat, fat, and meat byproducts of cattle, goats, hogs, horses, poultry, and sheep at 0.2 ppm; milk at 0.05 ppm and eggs at 0.2 ppm.

2. Valent U.S.A. Corporation proposes that 40 CFR 185 be amended to establish a food additive tolerance for the combined residues of the herbicide (E)-2-[1(((3-chloro-2-propenyl)oxy)imino)propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexene-1-one and its metabolites containing the 2-cyclohexene-1-one moiety on the following food commodities: soybean soapstock at 15.0 ppm and cottonseed meal at 2.0 ppm.

CB Comments

Deficiency 19 of our March 12, 1990 review is tentatively resolved. CB tentatively concludes that residues of total clethodim are not expected to exceed the above proposed tolerance from the proposed conditions of use of Select® Herbicide.

Judgment is deferred on the adequacy of these tolerances until there have been two successful PMVs.

PRODUCT CHEMISTRY

Deficiency (From our March 12, 1990 review)

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 DEB's companion review titled "PP#9F3743. Clethodim Product Chemistry Data submitted in Support of Registration," M. Nelson, DEB No. 5681, dated March 12, 1990, which see, for details.

Petitioner's Response

The petitioner has not responded.

CB Comments

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

cc: R.F., Circu (7), Review (FDG), PP#9F3743, D.A. Marlow (ACB/BEAD), C. Furlow (PIB/FOD).

H7509C:CB-I:Reviewer (FDG):CM#2:RM814B:557-0826:JOB: 55967:I:WP5.0:C.Disk:KENCO:10/25/90:DD:VO:EK:DD:ed:fdg:10/31/90.

RDI:SecHd:RSQuick:11/9/90:BrSrSci:RALoranger:11/9/90.