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B. Sidwell
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OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#3F4229/FAP#3H5674 Oxyfluorfen in or on Peanuts.
Amendment Dated 8/23/95 in Response to CBTS Review.
Review of Analytical Method and Residue Data. Rotational
Crops Data. Chemical No.: 11601, MRID Nos.: 405670-01,
437650-00 and 437568-02 through 05, CBTS Nos: 16179 and
16180, DP Barcodes: D218956 and D218957.

FROM: William D. Cutchin, *Bernard Schneider for WDC* Chemist
Tolerance Petition Team I
Chemistry Branch I - Tolerance Support
Health Effects Division (7509C)

THROUGH: Ed Zager, Acting Branch Chief
Chemistry Branch I - Tolerance Support
Health Effects Division (7509C)

RB Effects for

TO: Debbie McCall, Acting Section Head
Risk Coordination and Analysis Branch
Health Effects Division (7509C)

Executive Summary of Residue Chemistry Deficiencies

CBTS is recommending for time limited tolerances for the residues of oxyfluorfen *per se* on the raw agricultural commodities peanut nutmeat and hay at 0.05 ppm provided revised Sections B and F are submitted. In order to make the tolerances permanent, the following deficiencies need to be addressed.

Plant Analytical Method:

Clarification of Performing Laboratory and an ILV.

Animal Analytical Method:

Additional Data for Meat, Milk, Poultry, and Eggs Methods and an ILV.

Magnitude of Residue Data:

Fortification or Bridging Data in Support of Previously Submitted Peanut Residue Data and Clarification of Performing Laboratory.

Plant or Peanut Storage Stability Data.

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Background

Rohm and Haas Company responds to the deficiencies in the CBTS review (PP#3F4229/FAP#3H5674, DP Barcodes: D192408, D196984, D197110, W. Wassell, 5/12/94) of their petition requesting the establishment of tolerances for residues of the herbicide oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene] and its metabolites containing the diphenyl ether linkage in or on peanuts and peanut commodities. The registrant has responded to the review, submitted additional residue and rotational crop data, and now requests oxyfluorfen per se tolerances on the raw agricultural commodities peanut nutmeat and hay at 0.05 ppm and peanut hulls at 0.10 ppm. The petitioner also requests the establishment of oxyfluorfen food/feed additive tolerances in or on peanut meal and refined oil at 0.05 ppm.

Tolerances have been established for residues of oxyfluorfen and its metabolites containing the diphenyl ether linkage in or on various raw agricultural commodities from 0.05 ppm including pistachios, soybeans, grapes, milk and fat, meat, and meat byproducts of cattle, goats, hogs, horses, and sheep to 0.10 ppm on almond hulls and mint hay (40 CFR §180.381). Food additive tolerances of 0.25 ppm have been established for residues of oxyfluorfen and its metabolites containing the diphenyl ether linkage in or on the processed commodities cottonseed oil, mint oil (peppermint and spearmint), and soybean oil (40 CFR §185.4600).

Oxyfluorfen is a FIFRA '88 List B pesticide active ingredient and a Phase 4 Review of the chemical has been completed (S. Funk, 03/16/91).

Conclusions

1. ~~The data presented here is inadequate to fulfill the requirements of Guideline 62-3 regarding the precision and accuracy of the analytical methods for the impurities of the oxyfluorfen TGAI.~~ The data requirement remains outstanding for the purposes of reregistration. However it is not a deficiency for this petition.

2. The proposed use outlined in Section B is not adequate. The registrant has still included wording that implies postemergence applications of the product may be made. If growing season applications are intended, the registrant should submit residue data reflecting the use. Alternatively, the registrant must revise the sentence. See the "Proposed Use" section for suggested label text.

3. The nature of the residues of oxyfluorfen in plants and animals is adequately understood. The residue requiring regulation and to be included in the tolerance expression is parent only.

4a. The plant analytical method for oxyfluorfen per se is inadequate but upgradeable. The registrant must clarify what part or parts of the submitted validation study (on soybeans and grapes) and peanut residue trials were undertaken by the two performing laboratories. The registrant must also submit an independent laboratory validation (ILV) of the analytical method.

4b. The animal analytical methods are inadequate but upgradeable. The registrant must submit additional data (including radiovalidation) and a confirmatory procedure for the various methods and an ILV of the methods. Refer to the 11/15/94 and 12/19/95 S. Knizner reviews conducted in conjunction with reregistration for details.

5a. The magnitude of the residue data for oxyfluorfen on peanuts is inadequate. Since different analytical methods were used in the previous and new field trials, the petitioner must provide bridging data for the residue data previously submitted for peanuts. Alternatively, the petitioner could provide the additional recovery data requested previously for Method TR# 31C-87-16 (see 5/12/94 review of this petition) or conduct additional field trials using the new method for residues of oxyfluorfen per se. The petitioner must also clarify which part or parts of the studies submitted here were undertaken by the performing laboratories.

5b. As peanut hulls are no longer considered a significant livestock feed, hulls should be deleted from Section F.

5c. The registrant has proved by finding no residues on peanuts treated with oxyfluorfen at an exaggerated rate equal to the concentration factor for peanut processed commodities, that residues on peanut processed commodities are unlikely. A revised Section F is needed, deleting the food/feed additive tolerances for peanut oil and meal.

6. The storage stability data for oxyfluorfen on peanuts is inadequate. The registrant has submitted only a summary table of storage stability data. Until the data are received, reviewed, and found acceptable by CBTS, the deficiency remains.

7. The rotational crop data requirements for oxyfluorfen are being addressed by CBRS through reregistration. No rotational crop data are required for this petition.

8. The established tolerances for animal commodities do not need to be increased as a result of the proposed use on peanuts.

Recommendations

Provided the registrant submits revised Sections B and F (see conclusions 2, 5b, and 5c), CBTS recommends for time limited tolerances for the residues of oxyfluorfen per se on the raw

agricultural commodities peanut nutmeat and hay at 0.05 ppm. In order to make the requested tolerances permanent, the registrant should submit the data requested in 4a, 4b, 5a, and 6.

Note to PM: The registrant should be provided with a complete copy of this review.

Detailed Considerations

Manufacture and Formulation

The data presented as MRID# 427568-03 is inadequate to fulfill the requirements of Guideline 62-3 regarding the precision and accuracy of the analytical methods for the impurities of the oxyfluorfen TGAI. The registrant indicates that any further precision and accuracy data will be presented with the upcoming registration of the new process for the manufacture of the TGAI. CBTS concludes outstanding product chemistry deficiencies exist and data to fulfill Guideline 62-3 are still outstanding. However, this is not a deficiency for this petition.

Oxyfluorfen is formulated as Goal® 1.6E Herbicide (EPA Reg. No. 707-174), an emulsifiable concentrate containing 19.4% of the active ingredient (or 1.6 lbs ai per gallon of formulated product) and 80.6% of inert ingredients.

Proposed Use

The registrant has submitted a revised Section B. The proposed use of the product involves a single preemergence application following planting at a rate of 0.5 to 1.5 pints per acre (0.1 to 0.3 lbs ai/A) in a minimum of 20 gallons per acre. The following restrictions are included on the label: (a) Do not apply more than 1.5 pints (0.3 lbs active) of Goal 1.6E herbicide per acre per season; (b) Do not feed or graze animals on peanut fields treated with GOAL 1.6E herbicide until after harvest of the peanuts; (c) Chemigation: Do not apply this product through any type of irrigation system.

All of the Section B deficiencies pointed out in our previous review have been satisfied except one. The registrant has still included in the last sentence of the first paragraph under the "General Information" section wording that implies postemergence applications of the product may be made. If growing season applications are intended, the registrant should submit residue data reflecting that use. Alternatively, the registrant must rewrite the sentence in a revised Section B, eg. "For a full season weed control, timely cultivations and/or a postemergence weed control program, with products approved for the specific crop other than GOAL 1.6E, will assist in weed control."

Nature of the Residue

Animal metabolism data were not submitted with this petition. Two deficiencies from CBRS were cited in our original review concerning the ruminant metabolism study: the residues in goat liver were inadequately characterized and storage stability data were not provided. CBRS determined, after additional data were received, that the ruminant metabolism study was adequate except for storage stability requirements. The predominant goat liver metabolites identified were amino-oxyfluorfen and its conjugates and amino-hydroxy-oxyfluorfen and its conjugates (DP Barcode: D207134, MRID#s: 43307502, 43346401, 43307503, and 43317701, CBRS#s: 14321 and 14323, S. Knizner, 11/15/94). A storage stability study for meat, milk, and eggs was later received from the registrant and reviewed. CBRS determined that oxyfluorfen residues were stable in cow muscle and liver for up to 14 months and in milk and eggs for up to 12 months of frozen storage at -10 C. The study shows that oxyfluorfen is stable up to 12 months in frozen storage on muscle, liver, eggs, and milk (DP Barcode: D220695, MRID#: 43813201, CBRS#: 16436, S. Knizner, 1/2/96).

For both plants and animals, CBRS has concluded that the residue requiring regulation and to be included in the tolerance expression is parent only (S. Knizner, 4/7/94, CBRS#s: 12522, 13212, 12513, 13338).

Analytical Methods - Enforcement and Data Collection

Plants MRID#s 437568-04

An enforcement method for oxyfluorfen in plants (almonds, corn, grapes, soybeans, and stone fruit) is published in PAM Vol. II as Method I. This method determines levels of oxyfluorfen and its reduced metabolites by a common moiety method as a heptafluorobutyramido derivative of oxyfluorfen. This method was reviewed in conjunction with Phase 4 Review of the chemical and was considered adequate for Phase 5 review (see the oxyfluorfen Phase 4 Review of 3/16/91, S. Funk). However, as tolerances will be established on oxyfluorfen per se, this common moiety procedure will not be appropriate for enforcement purposes.

The registrant has submitted a new method, TR 34-94-150, which the registrant will rename TR 34-95-111 in 9/95, as the method for the determination of oxyfluorfen per se residues on plants. The procedure involves extraction of residues from plant matrices with acetonitrile. The extract is then further purified by liquid-liquid partition, silica gel column chromatography, and basic alumina solid phase extraction. The quantification of oxyfluorfen residues is done by gas chromatography using a Rtx-200, 60 meter column, and an electron capture detector.

The registrant has included a validation study showing recovery data using this method on soybeans and grapes (MRID# 437568-04). The average recoveries for fortifications from 0.01 to 0.5 ppm were $105\% \pm 11.3\%$ and $91\% \pm 10.5\%$ on soybeans and grapes respectively. A GC column analysis using a Rtx-50 on the same samples was used as a confirmatory method. This has been found by CBRS to be inappropriate and a GC/MS confirmatory method is in development (DP Barcode: D221731, CBRS#: 16622, S. Knizner, 12/19/95). The performing laboratories, Rohm and Haas Co. and Centre Analytical Laboratories, Inc., have submitted sample chromatograms and calibration curves. It is not apparent from the submission which lab performed which part or parts of the procedure. This must be clarified. An independent method validation (ILV) must be submitted followed by a tolerance method validation (TMV) in order for the method to be accepted as an adequate enforcement method in accordance with PR 96-1.

The registrant has included fortification and recovery data with new peanut residue studies using this method (MRID# 437568-05). The procedure is slightly different from that used in the grape and soybean study. The procedure involves extraction of residues from plant matrices with acetonitrile. The extract is then further purified by liquid-liquid partition, silica gel column chromatography (nutmeat), florisil column chromatography (vine, shell, hay) and basic alumina solid phase extraction. The quantification of oxyfluorfen residues is done by gas chromatography using a Rtx-200, 60 meter column, and an electron capture detector. The data indicate that recoveries from peanut matrices were adequate using the modified method. Oxyfluorfen recoveries from nutmeats fortified from 0.01 to 0.5 ppm were 98%, and vines, hay and shells fortified from 0.02 to 0.5 ppm were 75%, 90%, and 91% respectively. LOD's were 0.003 ppm for nutmeats and 0.007 ppm for vines, hay and shells. LOQ's were 0.01 ppm for nutmeats and 0.02 ppm for vines, hay and shells.

The performing labs conducting the residue studies, Rohm and Haas Co. and Centre Analytical Laboratories, Inc., submitted sample chromatograms and calibration curves. However, the peanut recovery data summarized by the registrant do not agree with the fortification recoveries presented with the residue trial data by the performing labs. The registrant must explain the discrepancy. Also, it is not apparent from the submission which lab performed which part or parts of the procedure. This must be clarified.

Included in the residue study was a log of method modifications used by the labs. Since this method is intended to be the enforcement for oxyfluorfen on plants, the registrant is instructed to make the needed revisions to the method and have the method validated by an independent laboratory to satisfy the requirements in PR Notice 96-1 for an ILV. If the ILV is found acceptable by CBTS, the method must undergo a successful tolerance method

validation (TMV) by the Agency in order to become an adequate enforcement method.

Animals

No new methodology for the determination of oxyfluorfen in animal tissues was included in this submission. An enforcement method for oxyfluorfen in animal matrices is published in PAM Vol. II as Method II. The Phase 4 Review of 3/16/91 requires the registrant to submit validation data for the determination of oxyfluorfen and the diphenyl ether metabolites in/on eggs and liver, since these data were not provided for this analytical method (S.R. Funk).

The registrant has submitted new analytical enforcement methods for meat, milk and eggs (DP Barcode: 207134, MRID#s: 43307502, 43346401, and 43307503, CBRS#s: 14321 and 14323, S. Knizner, 11/15/94). The submitted analytical enforcement meat/milk/egg methods are not adequate but are upgradeable. The majority of the deficiencies involve clarifications to the method or corrections for Branch policies. The only new data needed are radiovalidation of the method using egg samples from the metabolism study and development of a GC/MS confirmatory method or interference study (DP Barcode: D221731, CBRS#: 16622, S. Knizner, 12/19/95).

The registrant is reminded that after making the requested modifications, the methods must undergo independent laboratory validation (ILV) followed by Agency TMV as per PR Notice 96-1.

Storage Stability:

Storage stability data to support the magnitude of residue studies were not submitted in conjunction with this petition. CBRS received and reviewed a storage stability study for animal tissues. CBRS determined that oxyfluorfen residues were stable in cow muscle and liver for up to 14 months and in milk and eggs for up to 12 months of frozen storage at -10 C° (DP Barcode: D220695, MRID#: 43813201, CBRS #16436, S. Knizner, 1/2/96).

The registrant's summary tables indicate that oxyfluorfen residues are stable on plant matrices for up to 3 years. However, no storage stability data on plant matrices have been received to date. CBTS defers judgement on the acceptability of the studies until such time as plant storage stability data are submitted.

Magnitude of Residue - Crop Field Trials MRID No.: 437568-05

The registrant has submitted data from three additional residue trials on peanuts conducted in 1993 and 1994. The trials were conducted in Georgia, Oklahoma, and Virginia as requested in our original review (PP#3F4229/FAP#3H5674, DP Barcodes: D192408, D196984, D197110, W. Wassell, 5/12/94). Each trial had a single untreated control plot. The Georgia trial used a single

preemergence spray of oxyfluorfen on one plot at the label rate of 0.3 lb ai/A (1x) and on another plot at 0.9 lb ai/A (3x). The single preemergence application in Oklahoma and Virginia were at 0.5 lb ai/A (1.7x).

No residues were found on any nutmeat sample <0.02 ppm (LOQ) at any application rate. The shell and hay also exhibited no residue, <LOQ. The only quantifiable residue found was on a vine sample from Oklahoma at the LOQ, 0.02 ppm. Sample chromatograms and calibration curves from the residue study were provided by the performing laboratories, Rohm and Haas Co. and Centre Analytical Laboratories, Inc. It is not apparent from the submission which lab performed which part or parts of the procedure. This must be clarified.

The registrant has provided a table listing the dates of application, planting, digging of vines, green vine sampling, hay sampling, nut sampling, homogenization, extraction, and analysis for trials conducted in 1989 in AR, FL, GA (3), NC (2), VA (2) and TX. Also listed are the dates for the three trials which are reviewed in this submission designated as 93-0142 OK, 93-157 VA, and 94-0176 GA. The dates of the original trials show sampling to analysis intervals of 26-27 months. The dates of the residue studies included with the current submission show sampling to analysis intervals of 7-19 months. Homogenization to extraction and extraction to analysis intervals for all the trials were approximately 6 months and 1 week respectively. If the registrant's storage stability studies are deemed acceptable it would support the residue data from all the trials. The determination as to the acceptability of the storage stability studies will be made after they are received and reviewed.

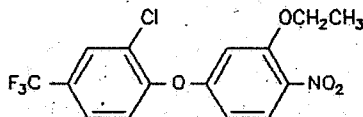
A revised table of the residues of oxyfluorfen on peanuts for the original trials was presented in the petition. The results have not been corrected for fortification recoveries. The highest residue found was for a Florida peanut hull sample at 0.077 ppm. Residues of oxyfluorfen were less than LOQ for peanut hay and vines. None of the treated samples of peanut nutmeats contained any oxyfluorfen residues (<LOQ). One control sample of nutmeat had 0.0281 ppm oxyfluorfen. These data were collected using the original residue method, TR# 31C-87-16.

The fortification studies on soybeans and grapes included in the petition (MRID# 437568-04) indicate the proposed new method will be adequate for data collection from plant matrices. (See Analytical Methods - Enforcement and Data Collection, Plants above.) The fortification and recovery data in/on peanut commodities generated using the new method and reported in the residue trials in this submission also support the registrant's contention that the method is adequate for data collection. Fortification data submitted for a new method will not support data from a previous method. Therefore, the additional recovery data requested for Method TR#

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Rotational Crop Data MRID 405670-01

The rotational crop study cited by the registrant has been reviewed by EFED and CBRS. Rotational crop data requirements will be addressed by CBRS as part of the reregistration process. No rotational crop data are necessary for this proposed use.

OXYFLUORFEN

cc: Cutchin, RF, Circ., PP#3F4229/3H5674, Oxyfluorfen List B
Reregistration file, B. Sidwell (SRRD, 7508W),
J. Miller/E. Wilson - PM-23 (7505C).

7509C: CBTS, Reviewer (WDC), CM#2, Rm 804P, 305-7990, WDC: 4/ /96
RDI: TPT1: 4/16/96;

Br. Sr. Sci.: R. Loranger: 5/ /96;
Act. Br. Ch.: E. Zager: 5/ /96.

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