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

FEB 6 1995

MEMORANDUM

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Subject: **CLETHODIM (SELECT®) ON POTATOES IMPORTED FROM CANADA.**
Review of Crop Field Trial Data.
(No MRID #)[CBTS # 15018]{DP Barcode 211445}

To: Anne E. Lindsay, Director
Policy and Special Projects Staff
Office of Pesticide Programs (7501C)

From: Francis D. Griffith, Jr., Chemist
Chemistry Branch I - Tolerance Support
Health Effects Division (7509C)

Thru: E. Zager, Acting Branch Chief
Chemistry Branch I - Tolerance Support
Health Effects Division (7509C)

BACKGROUND

Clethodim residues on potatoes grown in Canada and imported into the USA have been identified as a Canada-United States Trade Agreement (CUSTA) trade irritant. PSPS has requested CBTS review the Canadian crop field trial residues data to ascertain whether it is adequate to support an "import" tolerance.

There is no formal pesticide petition associated with this review.

RECOMMENDATION

CBTS could recommend for the clethodim and its metabolites containing the 2-cyclohexen-1-one moiety tolerance at 0.5 ppm on potatoes and 1 ppm FAT on potato flakes/granules as total clethodim residues are not expected to exceed these values when Select Herbicide is used as described in the field trials and stated in D. Cosgrove report dated march 30, 1992. A DRES analysis using these residue levels can be initiated.

If a tolerance regulation is promulgated in 40 CFR §180.458, then it should bear the notation that there are no USA registrations for use of clethodim on potatoes as of (the date for the Regulation).

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DISCUSSION - CONCLUSIONS

PRODUCT CHEMISTRY/CHEMICAL IDENTITY

A letter was submitted that states Tomen Pacific Agro Co. is the manufacturer of clethodim for both Valent USA and Rhone-Poulenc Canada. Since an adequate product chemistry data base has been submitted in PP# 9F3743 and there have been no revisions to these data, the impurities associated with the TGAI when formulated into Select and used as directed are not expected to be a residue problem in potatoes imported from Canada.

DIRECTIONS FOR USE

No label for Select Herbicide showing directions for use on potatoes in Canada was submitted. However, the use pattern can be determined from the crop field trial reports, and from the D. Cosgrove report dated March 1992 indicating that the use is to reflect a maximum proposed label rate of 0.375 l/ha (90 grams a.i./ ha) with a 60 day PHI.

NATURE OF THE RESIDUE - PLANTS AND LIVESTOCK

^{14}C-clethodim metabolism studies in carrots, soybeans, and cottonseed were submitted (ibid). In summary, the major plant metabolic pathway is sulfoxidation to form clethodim sulfoxide and further oxidation to form the clethodim sulfone, and hydroxylation to form both the 5-OH sulfoxide and 5-OH sulfone. There is cleavage of the oxime N-O bond and elimination of the chloroallyoxy side chain to form the imine sulfoxide and sulfone. The sulfoxides and sulfones form conjugates.

^{14}C-clethodim metabolism studies for goats and hens were submitted (ibid). In summary, clethodim metabolism in hens involved only the sulfoxidation to the sulfone and sulfoxide. In goats not only this pathway exists, but also clethodim converted to the S-methyl with oxidation to form the S-methyl sulfoxide and S-methyl sulfone, and the oxime N-O bond cleaved to produce the imine, and then the imine sulfoxide. Hydroxylation at the 5 position is a minor pathway in goats.

The nature of the residue in plants and livestock is adequately understood. The residues of concern are clethodim and its metabolite containing the 2-cyclohexen-1-one moiety.

ROTATIONAL CROPS

Rotational crops studies, either confined or field, are not required for import tolerances.

STORAGE STABILITY

Freezer storage stability data have been submitted that show total clethodim residues (clethodim, and its sulfoxide and sulfone plus the 5-OH metabolites) are stable at -20°C in soybeans and

cottonseed for at least 6 months (ibid), and in onions and sugarbeets for 12 months (see PP# 4F4340). These data can be translated to support the storage of potatoes for the same length of time.

RESIDUE ANALYTICAL METHODS

There are adequate multiresidue method (MRM) and independent laboratory validation (ILV) data available for clethodim and its metabolites (op.cit).

There are adequate residue analytical methods available to enforce the 0.5 ppm total clethodim tolerance on potatoes. Both methods have successfully completed TMVs in the Agency's laboratories. The primary enforcement method is Valent method EPA-RM-26D-1 which can separate clethodim from sethoxydim and is a HPLC-UV procedure. To confirm total clethodim residues there is a common moiety method, Chevron method RM-26B-2, which converts the residues to dicarboxylic acids, and after methylation determination is by GC-FPD in the sulfur mode. The LOQ is 0.05 ppm in crops and tissues, and 0.02 ppm in milk. The MDL is 0.03 ppm in crops and tissues. Both methods have been forwarded to FDA for publication in a future edition of PAM II. The common moiety method cannot distinguish between clethodim and sethoxydim residues.

The magnitude of the residue data for potatoes in Canada were gathered by an earlier version of the common moiety method, method RM-26A-1. Basically this is the same method currently in PAM II for the determination of sethoxydim residues. Huntingdon Analytical Services (HAS) has provided adequate concurrent clethodim sulfoxide and 5-OH clethodim sulfone method validation data by spiking control samples at 0.05 (LOQ), 0.1, 0.5 (proposed tolerance), and 1 ppm levels. Clethodim sulfoxide recoveries ranged from 61.1% to 128.6%, averaging 78%, and 5-OH clethodim sulfone recoveries ranged from 59.95 to 113.6%, averaging 79%. Method RM-26A-1 is suitable to gather the clethodim in potatoes crop field trial residue data.

The appropriate reference analytical standards to validate these procedures as enforcement methods are available from EPA's Pesticide Repository in RTP, NC.

MAGNITUDE OF THE RESIDUE - CROP FIELD TRIALS

Crop field trial data were presented in a study titled "Herbicides:Clethodim:Select® Residue Studies in Potatoes, Canada, 1990-91" by D. Cosgrove and dated March 1992. The title page was stamped TRADE SECRET, confidential, proprietary data of Rhone-Poulenc Canada, Inc. Only the analytical phase contained a GLP statement.

12 potato field trials for the 1990-1991 crop years using 7 varieties were conducted in Ontario (5), Nova Scotia, Prince Edward Island, Quebec (2), Manitoba, Alberta, and Saskatchewan Canada. There are adequate varietal and geographical representation for an import tolerance.

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Select Herbicide, an emulsifiable concentrate, containing 240 grams/liter ai clethodim was applied to potatoes at the flowering stage one time at a rate of 375 ml/ha or 90 grams ai/ha (approx. 0.08 lb ai/A) using ground equipment. An adjuvant, CC 16233 was added to the spray solution at a rate of 1% v/v. RD should determine if the adjuvant is cleared under 40 CFR §180.1001 for use on crops.

A double application (2X) was applied to another plot to simulate field overlap conditions. Samples were harvested at 44-46 days and 59-61 days with 60 days being the recommended PHI. Samples were collected from both the control and treated plots at each test site and from at least 6 plants. A 2 kg composite representing at least 6 potatoes were frozen and retained until analysis.

Samples were analyzed in duplicate at HAS within 3-4 months of harvest. All of the results with supporting data were reported. Control potato samples showed total clethodim residues to <0.05 ppm. Total clethodim residues at 60 days PHI from the 90 g ai/ha application ranged from <0.05 ppm (n = 15) to 0.34 ppm, averaging 0.09 ± 0.1 ppm; and from the 180 g ai/ha (2X) application residues ranged from < 0.05 ppm (n = 8) to 0.74 ppm, averaging 0.22 ± 0.26 ppm. At 45 days PHI total clethodim residues for the 90 g ai/ha application ranged from <0.05 (n = 15) to 0.46 ppm averaging 0.11 ± 0.13 ppm, and from the 180 g ai/ha application total clethodim residues ranged from <0.05 (n = 7) to 0.85 ppm averaging 0.21 ± 0.23 ppm.

These data support a 0.5 ppm tolerance. When Select EC is applied at a rate of 90 g ai/ha to potatoes with a 60 day PHI total clethodim residues are not expected to exceed the 0.5 ppm tolerance.

MAGNITUDE OF THE RESIDUE - PROCESSED FOOD/FEED

No processing studies data were presented. In PP# 7F3529 a potato processing study was presented for a closely related herbicide sethoxydim. Potatoes bearing sethoxydim residues were processed using standard commercial potato processing practices and residues were found to concentrate in potato flakes and granules, but not potato chips or in processed potato waste. These data can be translated to show that a food additive tolerance on potato flakes and granules at 1 ppm is necessary. [redacted]

MAGNITUDE OF THE RESIDUE- MEAT/MILK/POULTRY/EGGS

Bovine feeding study has been conducted with the feeding of total clethodim residues up to 100 ppm in the diet (op.cit.). Cull potatoes and processed potato waste can be up to 75 % of beef cattle diets and up to 50% of dairy cattle diets. Finite total clethodim residues will actually occur in meat and milk from the feed use of clethodim treated raw agricultural commodities and/or their processed feed items. The established secondary total clethodim tolerances in

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milk and in meat, fat, and meat byproducts of cattle, goats, hogs, horses, and sheep remain adequate for this additional use.

There are no poultry feed items associated with potatoes. Secondary total clethodim tolerances have been established in eggs and in meat, fat, and meat by-products of poultry which are adequate to cover any inadvertent feed use of clethodim treated potatoes to poultry.

HARMONIZATION OF TOLERANCES

An INTERNATIONAL RESIDUE LIMIT status sheet is attached. There will be no problem in harmonizing with Canada's recently established 0.5 ppm total clethodim tolerance on potatoes. The 0.5 ppm total clethodim tolerance on potatoes cannot be harmonized with either the Codex expression or the numerical value at this time. It is possible that the 1991 Canadian field trial data were not available to Codex.

ATTACHMENT: INTERNATIONAL RESIDUE LIMIT STATUS SHEET

cc:R.F., Circu.,Reviewer(FDG),PM-21,ClethodimSub.File,DRES(B.Doyle-SAB), D.Edwards(RCAB).

7509C:CBTS:Reviewer(FDG):CM#2:Rm804Q:305-5826:FDG:1/30/95:edit:fdg:2/6/95.
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