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

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

JUL 16 1986

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MEMORANDUM

SUBJECT: PP#6F3383 (RCB No. 878) Sethoxydim (POAST®) In/On Strawberries and Raspberries - Evaluation of Analytical Methodology and Residue Data Accession No. 261890

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and

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THRU: Charles L. Trichilo, Chief
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BASF Wyandotte Corporation proposes the establishment of a permanent tolerance for combined residues of the herbicide 2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one and its metabolites containing the 2-cyclohexen-1-one moiety (calculated as the herbicide) on the raw agricultural commodities strawberries and raspberries at 10.00 ppm.

Permanent tolerances have been established on cotton, soybeans, sugar beets, and animal commodities at levels ranging from 0.05 to 15.0 ppm (40 CFR 180.412).

Permanent tolerances are pending for residues of sethoxydim on sunflowers and peanuts (PP#5F3234, M. Firestone, July 17, 1985), tomatoes and tomato products (PP#5F3284, C. Deyrup, October 9, 1985), and soybean and alfalfa, hay and forage (PP#3F2904, S. Malak, June 23, 1986).

Conclusions

1. The petitioner will need to specify the method of application used in his field trials. If the residue data do not reflect the proposed use of application by both air and ground equipment, then the petitioner will have the option of submitting the appropriate data or revising the Section B labeling to comply with that method of application used in his field trials.

2. Residue Chemistry Branch (RCB) concludes that the nature of the residue in strawberries and raspberries is adequately understood. The residues of concern are sethoxydim and its metabolites containing the 2-cyclohexen-1-one moiety.

3. Adequate analytical methodology is available for enforcement purposes.

4a. Storage stability of sethoxydim in strawberries, under freezer conditions, exhibited no determinable loss of the parent or metabolites over a 31-month period. These data adequately support the storage and handling of field samples.

4b. The residue data presented are not reflective of the proposed use and/or are insufficient in number and correlatable parameters to establish a residue level of sethoxydim for tolerance purposes. Sufficient residue data reflecting the proposed label rate and preharvest interval (PHI) are not presented and it seems that the proposed 10 ppm residue level is too high for a tolerance based on the presented data.

Additional residue data reflecting the proposed use, are required or the Section B/label should be revised wherein there is a better reflection of the residue data presented (see the Residue Data section of this review for more details).

5. Since strawberries and raspberries are not fed to livestock or poultry, secondary residues in meat, milk, poultry and eggs would not be expected to result from the proposed use.

6. No international (Codex) tolerances have been established for residues of sethoxydim in strawberries or raspberries. Thus, there will not be a compatibility problem. An International Residue Status sheet is attached.

Recommendations

RCB recommends against establishing permanent tolerances for residues of sethoxydim and its metabolites in/on strawberries and raspberries until the deficiencies described above in conclusions 1 and 4b are resolved.

Detailed Considerations

Manufacture and Formulation

The manufacturing process of sethoxydim was discussed in RCB's review of PP#0G2396 (memorandum of E. Zager, December 4, 1980). The technical product is > 94.9 percent pure. The impurities are not expected to present any residue problems.

The formulation to be used on strawberries and raspberries, Poast®, an emulsifiable concentrate, contains 20.0 percent by weight active ingredient. The inerts have been cleared under 40 CFR 180.1001.

Proposed Use

Applications of Poast are timed according to the size of the grass weeds present. In general, three applications are made to actively growing weeds as indicated in the three tables on the label, each table being representative of one of three growing regions in the United States. The growing regions are as follows:

Region 1 = California, Arizona, and western New Mexico
Region 2 = High rolling plains of Texas, Oklahoma and eastern New Mexico
Region 3 = Midwest, Mountain (except Arizona and New Mexico), South, Northeast and Pacific Northwest

The rate of application is 0.5 lb ai/A, 2 1/2 pints of Poast, with a maximum total per growing season of 7 1/2 pints or 1.5 lb ai/A, for strawberry and raspberry weed control. Each application must include 2 pints of nonphytotoxic oil concentrate per acre.

The labeling indicates that applications may be made through air or ground equipment. The last application of Poast must allow a 10-day interval before harvest (PHI).

Nature of the Residue

No metabolism data were submitted with this petition. C^{14}-sethoxydim has been successfully studied in tomatoes (PP#5F3284, C. Deyrup, October 9, 1985); in soybeans and alfalfa (PP#3F2904, K. Arne, June 26, 1985); and in sugar beets (PP#3F2950, K. Arne, February 2, 1984). Metabolism of sethoxydim yields a myriad of products of which six were identifiable in tomatoes, and alfalfa, nine were identifiable in soybeans, and four were identifiable in sugar beets. In each of these dissimilar crops the identified metabolites were common to each plant or identifiable as being derived by a common pathway of degradation. All metabolites contained the 2-cyclohexen-1-one moiety.

RCB concludes that the nature of the residue in strawberries and raspberries is adequately understood for the purposes of this proposed use. The residues of concern are sethoxydim and its metabolites containing the 2-cyclohexen-1-one moiety.

Analytical Methodology

The analytical methods used to determine residues of sethoxydim in strawberries and raspberries are designated as BASF Agricultural Chemicals Method No. 30B or 30G. The 30G method was used for alfalfa and reviewed in PP#3F2904 (K. Arne, June 26, 1985). The 30B method is similar to the 30G method and was the subject of a successful method trial on beef liver and soybeans (PP#2F2670, memorandum of K. Zee, April 1, 1983).

Strawberry and raspberry samples were analyzed according to the methodology used for soybeans and alfalfa. In brief, the method consists of extracting the sample with methanol, precipitating protein with $Ca(OH)_2$, partitioning the acidified filtrate with methylene chloride, concentration of the organic layer and oxidation of the residue with H_2O_2 in the presence of $Ba(OH)_2$ to give the substituted pentanedioic acids, and formation

of the corresponding methyl esters (DME and DME-OH) with methanolic hydrogen chloride. The esters are cleaned-up on a silica gel column and quantitated with GC/FPD in the sulfur mode.

The sensitivity of the methodology used for determining sethoxydim residues in strawberries and raspberries is given as 0.05 ppm. Recoveries of parent and the two major metabolites are as follows:

Sample Matrix	Fortification Compound	Fortification Range (ppm)	Average Recovery (%)
Strawberries	Sethoxydim	0.05-10.0	95.2
Strawberries	MSO	0.05-10.0	94.9
Strawberries	5-OH	0.05-10.0	84.2
Raspberries	Sethoxydim	0.05-5.0	95.3
Raspberries	MSO	0.05-5.0	95.7
Raspberries	5-OH	0.05-5.0	87.3

RCB concludes that adequate analytical methodology is available for regulatory purposes.

Residue Data

Storage Stability:

A study of storage stability was made using strawberry samples, field harvested in 1982, containing an analyzed level of sethoxydim and metabolites. A subset of these samples were stored for 31 months following the initial analysis, under freezer storage conditions. Fortified samples were analyzed for recovery determinations in 1982 and a subset was also stored for analysis in 1985.

Analysis for sethoxydim and 5-OH-MSO_2 at fortification levels of 0.05 to 5.0 ppm were 91 percent and 90 percent, respectively, in 1982, and in the 1985 analyses the recoveries were 96 percent and 111 percent, respectively. The field samples (containing weathered residues) upon reanalysis in 1985 (31 months) following freezer storage, resulted in average values of 117 percent for sethoxydim and 83 percent for 5-OH-MSO_2, based on the original (1982) analytical result.

It is concluded from these data that residues of sethoxydim in strawberry samples stored under freezer conditions for 31 months are sufficiently stable as both fortified or field weathered residues.

Strawberries:

Approximately 26 trials were performed in 9 States over a period of June 1982 to June 1983. Rates of application varied from 0.25 to 1.0 lb ai/A and number of applications from one to four. Sampling interval (PHI) from last application to harvest ranged from 4 to 331 days. However, residue data near the proposed use (0.5 lb ai/A, three applications and 10 days PHI) are presented, only, in two dissipation studies, from Minnesota (three 0.5 lb ai/A applications at 7-day PHI) and Michigan (three 0.5 lb ai/A applications at 9-day PHI).

Strawberry residue data are summarized below:

State	Treatment (lb ai/A)	Sampling Interval, days	Total Residues ppm
MN	0.5	42-52	0.34-0.54
MN	0.5 + 0.5	28-331	< 0.1-2.5
MN	0.5 + 0.5 + 0.5	4	3.3
MN	0.5 + 0.5 + 0.5	7	2.8
MN	0.5 + 0.5 + 0.5	31-38	0.41-0.54
MI	0.5	36-56	< 0.1-0.46
MI	0.5 + 0.5	27-42	0.36-1.5
MI	0.5 + 0.5 + 0.5	5 and 9	2.6 and 1.0
MI	0.5 + 0.5 + 0.5	38-47	0.21-0.55
FL	0.5	1 and 18	< 1 and 0.48
CA	0.5	15-34	0.36-1.6
OR	0.5 and 1.0	38 and 71	0.86 and 2.4
WI	0.25 (2X)	49-56	< 0.1
WI	0.25 (4X)	49-56	< 0.1
WI	0.5 (2X)	49-56	< 0.1
WI	0.5 (4X)	49-56	< 0.1
WI	1.0 (2X)	49-56	0.13-0.18
VA	0.5	70	< 0.1
NC	0.25-0.5 (3X)	304	< 0.1
NJ	0.5	19-21	1.8-3.6

These data are insufficient to correlate, extrapolate or interpolate, statistically or otherwise, for establishing or predicting a residue level for tolerance purposes, according to the proposed use on the label. A label change in keeping with the field trial data (i.e., 0.5 lb ai/A, single application, with a PHI of 30 days or more) might lend itself to determining a residue level for tolerance. To do tolerance estimation for the use as proposed in this petition, trial results would be needed, according to label use, in all States and additional dissipation studies (as were done in Michigan and Minnesota) should be performed in Florida, California, and Oregon or Washington and in one other State (New York, New Jersey, Pennsylvania or Ohio). The geographic distribution of the residue trial data are excellent, but the total data are not representative of the intended or proposed label use.

Raspberries:

Sixteen residue trials in five States produced no detectable residues (< 0.10 ppm) in four trials at proposed label rate (3 x 0.5 lb ai/A) with PHI's of 32 to 41 days; no detectable residues (< 0.1 ppm) in 10 trials at less than label rate (2 x 0.5 lb ai/A) with PHI's of 13 to 32 days; in two trials (California), residues of 1.7 ppm at a 26-day PHI following the label rate (3 x 0.5 lb ai/A) and 1.3 ppm at a 31-day PHI following an application of 2 x 0.5 lb ai/A.

These data show a distinct difference in residue levels between strawberries and raspberries which would certainly be expected from application of a herbicide to two perennial plants having such a difference in root to fruit systems.

Unfortunately, there are no data presented that are truly reflective of the proposed use (10-day PHI). Dissipation studies (as in strawberries, above) will be needed, according to the proposed use, at permissible sampling intervals (including the labeled PHI) in California, Michigan, and Oregon. If a 10-day PHI is desired, data from all five States (California, Michigan, Washington, Oregon, New Jersey) will be needed; these data need to be reflective of the proposed use. Perhaps a change in the PHI (revised Section B) will be feasible, dependent on the dissipation study data.

All of the data presented have no indication of the method of application (air or ground). Such information is required to substantiate the labeling or a change in the Section B label will be needed.

Of the data presented, no determination is possible regarding the adequacy of the proposed tolerance, 10 ppm in strawberries and 10 ppm in raspberries, for the proposed use. A revised Section F might be indicated, based on the additional new data required for further evaluation of this request.

Meat, Milk, Poultry, and Eggs:

Strawberries and raspberries are not used for feed or forage in livestock or poultry. Therefore, no secondary residues of sethoxydim in meat, milk, poultry, or eggs would be expected to result from the proposed use.

Attachment

cc:Circu, RF, Reviewer, PMSD/ISB, PP#6F3383, EEB,EAB,FDA
RDI:JHOnley-7/7/86:7/7/86-RDSchmitt
TS-769:RCB:CM#2:VFBoyd:RM1810:X77484
Edited by:Mimi/7/14/86

Attachment #1

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Sethoxydim

PETITION NO. PP#6F3383 BOYD 6/26/86

CCPR NO. _____

J. Knox 6/27/86

Codex Status

Proposed U.S. Tolerances

[✓] No Codex Proposal Step 6 or above

Residue (if Step 9): _____

Residue: PARENT PLUS 2-cyclohexeno-1-one containing metabolites

Crop(s) Limit (mg/kg)

Crop(s) Tol. (ppm)

STRAWBERRY 10.0
RASPBERRY 10.0

CANADIAN LIMIT

Residue: _____

Crop Limit (ppm)

none (on above commodities)

MEXICAN TOLERANCIA

Residue: _____

Crop Tolerancia (ppm)

none

NOTES: