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

FEB 7 1984

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#3F2934, (Acc. #071761).
Vinclozolin in or on Onions, Lettuce and
Raspberries. Evaluation of Residue Data
and Analytical Methodology.

FROM: Jesse E. Mayes, Chemist 
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

THRU: Charles Trichilo, Chief 
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TO: Henry Jacoby (PM-21)
Registration Division (TS-767)

and

Toxicology Branch
Hazard Evaluation Division (TS-769)

The petitioner, BASF Wyandotte Corporation, proposes to establish a tolerance for combined residues of the fungicide, 3-(3,5-dichlorophenyl)-5-ethenyl-5-methyl-2,4 oxazolidinedione (vinclozolin) and its metabolites containing the 3,5-dichloroaniline moiety in or on the raw agricultural commodities leaf lettuce and raspberries at 10 ppm and onions, green and dry bulb, at 1.0 ppm. Tolerances have already been established for residues of vinclozolin in or on kiwi fruit, strawberries and head lettuce at 10 ppm (§180.380). Tolerances are pending for residues in or on peaches and cherries at 4 ppm and plums at 1.0 ppm (2F2650); tomatoes at 2 ppm and cucumbers at 1.0 ppm (4F2998).

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Conclusions

1. The nature of the residue is understood. The residues of concern are the parent and metabolites containing the 3,5-dichloroaniline moiety.
2. Satisfactory analytical methods are available for enforcement of the proposed tolerances.
- 3a. Data on raspberries show high and erratic control values which question the reliability of the empirical data. It must be shown that the apparent inadvertent residues in plots do not adversely affect sample results causing higher residues. More data on raspberries are needed, reflecting the proposed use. Data for one plot indicate that the proposed tolerance could be exceeded. Wider geographical representation is also needed.
- 3b. Data reflecting the proposed use on leaf lettuce were collected only in the state of New Jersey. More geographical representation is necessary to make a judgment on the expected residues from this use.
- 3c. More data are needed on onions reflecting the proposed use and a wider geographical representation is necessary.
4. Since no feed items are involved in the proposed use, we do not expect any secondary residues to occur in meat, milk, poultry or eggs.
5. There is no problem with Codex compatibility.

Recommendations

We recommend against the proposed tolerance because of conclusions 3a, 3b, and 3c. For a favorable recommendation, the petitioner will have to resolve these deficiencies.

Detailed Considerations

Formulation

A detailed description of the manufacturing process is contained in PP#9F2205, Acc. #098253 (memo of July 23, 1979, M. Nelson). The technical product is listed as a minimum of 93% pure vinclozolin. None of the impurities in the technical product are expected to present any residue problems at the levels present.

The product is formulated as a 50% wettable powder under the trade name Ronilan Fungicide (50W), EPA Registration No. 7969-53. The inert ingredients listed in the statement of formula are all cleared in 40 CFR 180.1001.

Proposed Uses

Ronilan is a contact fungicide used to control the following fungi: (1) sclerotinia "drop" (watery soft rot) of lettuce; (2) botrytis fruit rot of raspberries; and, (3) sclerotinia watery soft rot, sclerotinia white rot, botrytis neck rots and botrytis leaf blight of onions, are as follows:

Leaf Lettuce: Up to 3 applications may be made at rates of 1-2 lbs. product per acre with a PHI of 28 days. Ground or air equipment may be used.

Raspberries: Applications may be made beginning at or before 10% primary bloom and subsequently at 7-14 day intervals at rates of 1-2 lbs. product per acre. The maximum poundage per season is 8 lbs. The recommended PHI is 9 days. Ground or air equipment may be used.

Onions: For control of soil-borne diseases, a combination of 1 soil treatment plus up to 4 foliar treatments directed at the stem base may be made at a rate of 2 lbs. product per acre. To control botrytis leaf blight, up to 5 foliar applications may be made at 1 1/2 - 2 lbs. product per acre. The maximum poundage per season is 10 lbs. The recommended PHI is 18 days. Ground equipment is used.

Nature of Residues

Metabolism studies have been reviewed with earlier petitions: PP#8G2068, Acc. #096965 (memo. of January 19, 1979, G. Makhijani) and PP#9 F2205, Acc. #098254 (memo. July 23, 1979, M. Nelson). Studies were conducted using ¹⁴C ring-labeled vinclozolin on strawberries, grapes, lettuce, peaches, soil and rats. In all of these studies the metabolic products contained the 3,5-dichloroaniline moiety which is determined by the analytical method. (A schema of the metabolic pathway based on the above studies can be found with PP#'s 8G2068 and 9F2205). We do not expect the metabolism of vinclozolin to vary appreciably in leaf lettuce, raspberries and onions.

We consider the plant metabolism of vinclozolin adequately understood. The residues of concern are the parent and metabolites containing the 3,5-dichloroaniline moiety.

Analytical Method

The analytical method involves an alkaline hydrolysis of parent and acid metabolites that releases 3,5-dichloroaniline which is collected in a 1 N sulfuric acid solution during steam distillation. The 3,5-dichloroaniline in aqueous solution is partitioned with dichloromethane in a cleanup step followed by derivitization with chloroacetyl chloride. The chloroacetyl derivative is determined by gas chromatography using a ⁶³Ni electron capture detector.

Reported recovery studies were as follows:

Commodity	Fortification Range (ppm)	% Recovery Range	# Recoveries	Avg % Recovery
Caneberries	0.05-20.0	56-109	38	81
Leaf Lettuce	0.1-5.0	60-104	18	79
Onions	0.05-2.0	80-100	24	88

The method is sensitive to 0.05 ppm.

The method used for determining these residues is essentially the same as that subjected to a method trial (Method No. 25, dated November 21, 1977) on strawberries. Only a few minor changes were made which we would not expect to vary the recoveries substantially.

Studies were conducted to determine specificity of the analytical method for determining residues of the 3,5-dichloroaniline moiety in the presence of other pesticides

approved for use on canberries (incl. raspberries), onions and leaf lettuce. The approved pesticides were added to the commodities prior to the alkaline hydrolysis step and the procedure continued through to the gas chromatographic determinative step. The reported results indicate that none of the currently available pesticide compounds registered for use on one or more of these commodities would interfere with the GLC determination of vinclozolin or any of its metabolites containing the 3,5-dichloroaniline moiety.

We conclude that adequate analytical methodology is available for enforcement purposes.

Residue Data

Residue studies were conducted in small scale research plots reportedly because an EUP was not requested. The petitioner indicates that due to the closeness of the controls to treated crops that there could be contamination of control samples. The results do indicate that control samples were contaminated.

Samples were packed in dry ice upon collection and remained frozen until analysis. None were stored longer than one year. A storage stability study was reviewed in connection with PP#'s 8G2068 and 9F2205 (Acc. #096965 and 098254 respectively). The study showed that both vinclozolin and its metabolites containing the 3,5-dichloroaniline moiety were stable in strawberries at -15°C for up to 19 months. Recoveries averaged $88 \pm 11\%$ for parent compound and $94 \pm 15\%$ for the metabolites.

Raspberries

Residue studies were conducted with red raspberries in the states of MI, OR, OH and WA in the growing season of 1982. A total of 56 treated samples and 29 controls were collected from plots in these four states (two locations in the state of WA). Treatments ranged from 0.75 lb. ai/A (0.75x) to 1.5 lb. ai/A (1.5x). The number of applications ranged from 3 to 5 per season and PHIs ranged from 0-39 days.

Only in one study was the maximum recommended rate of 1 lb. ai/A with 4 applications followed (Williamston, MI). This study was paralleled with a rate of 0.75 lb. ai/A. In this case the PHIs were 0, 1, 3, and 7 days. Residues ranged from 1.6 ppm for 7 days PHI (0.75 lb. ai/A) to 4.2 ppm 0 days PHI (0.75 lb. ai/A).

Treatment Rates	No. of Applications	PHI Days	BAS 352F equivalents	Total Residues
0.75	3	4	10.7	
0.75	3	4	6.6	
0.75	3	4	3.5	
0.75	3	4	12.4	<u>33.2 ppm</u>
1.5	3	4	15.1	
1.5	3	4	5.1	
1.5	3	4	10.2	
1.5	3	4	9.5	<u>39.9 ppm</u>

As shown in these data, a 2x application yielded only 17% higher residues in the treated crop. This analysis would indicate that either the experimental process was faulty or due to the small amounts of pesticides applied, the variability of conditions could produce apparently aberrant results. Whereas neither of these indications is conclusive, we do believe that for the purpose of determining expected residues from a maximum recommended use of 4 lb. ai/season, we can use data resulting from a seasonal application of 4.5 lbs. ai.

Also, data from Williamston, MI; Hillsboro, OR; Lynden, WA and Puyallup, WA were plotted on a graph to determine the relative amount of residue to expect for 9 days PHI compared to 4 days PHI. The plots showed roughly that 63% to 83% of the residue present at 4 days PHI would be present at 9 days PHI.

Using these percentages for the above data, the high residue expected at 9 days PHI would be 9.5 (15.1 x 0.63) to 12.5 ppm (15.1 x 0.83). Hence a higher tolerance level would be required.

Control samples were erratic and generally of high values. The petitioner indicated that the plots were close together and that the possibility existed for inadvertent transfer of pesticide to untreated plots. Control samples ranged up to 3.7 ppm. The petitioner indicates that the GLC response for control samples shows that it is clearly Ronilan (or a metabolite containing the 3,5-dichloroaniline moiety). This, again, causes some concern about the adequacy of the proposed tolerance level. By the control samples being of erratic values, we can not reliably estimate what residues are due to purposeful use and what is due from inadvertent contamination.

Leaf Lettuce

Residue studies were conducted in two States, NJ and NY.

Only six studies used the maximum recommended rate of 3 applications of 1 lb. ai/A. A summary of these results is shown in the following table.

<u>Location</u>	<u>Crop</u>	<u>Rate</u> (lb. ai/A)	<u>No. Appl.</u>	<u>PHI</u> (days)	<u>Residue</u> (ppm)
NJ	Leaf Lettuce	1	3	10	0.85
NJ	Leaf Lettuce	1	3	11	0.32
NJ	Romaine	1	3	11	0.55
NJ	Escarole	1	3	12	0.62
NJ	Escarole	1	3	12	0.65
NJ	Chicory	1	3	22	0.45

As shown in the table, only one State is involved in the study. It does not appear from these studies that the proposed level of 10 ppm will be exceeded from the proposed use. However, we do not feel that we have adequate geographical representation. Thus, we can not conclude that the proposed tolerance will not be exceeded in all growing areas.

The highest residue found was in a study on escarole: two applications of 1 lb. ai/A with a PHI of 11 days yielded 5 ppm (5.5 & 50. dup. anal.).

Onion

Residue studies were conducted in three states, MI, NJ, and OR. A total of 40 treated samples and nine controls were reported. The proposed use allows up to 5 lb. ai per growing season to be applied. In only one study in MI was this amount applied. Nine treatments of 0.75 and 1 lb. ai/A were made with 13 days PHI. The residues found for these two treatments were 0.05 and 0.06 ppm.

The highest values found were in a study in NJ. Up to 0.65 ppm were found resulting from 2 applications of 0.75 lb. ai/A to foliage with a 34-day PHI. At the maximum poundage of 5 lb. ai per season and a PHI of 18 days, the level could conceivably be above the proposed 1 ppm.

Additional studies should be submitted which reflect the proposed use. Also, more representative geographical locations should be required.

Meat, Milk, Poultry and Eggs

Since no feed items are involved in the proposed use we do not expect any secondary residues to occur in meat, milk, poultry or eggs.

Other Considerations

There is no problem with Codex compatibility. There is no Codex proposal for vinclozolin above step 6. (See attached "International Residue Limits Sheet.")

cc: R.F.
Circu
Reviewer

TOX

EEB

EAB

Petition No 3F2934

FDA

Robert Thompson

RDI:Section Head:AS>Date:1/26/84:RDS>Date:1/26/84

TS-769:RCB:Reviewer(JEM):Typist (mar)RM:810:CM#2>Date:(2/1/84)

DCR-34341

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Vinclozolin

PETITION NO. 3F2934

CCPR NO. _____

Reviewer Jesse E. Mayer
J. E. 11/17/83

Codex Status

No Codex Proposal
Step 6 or above

Proposed U. S. Tolerances

Residue. 3-(3,5-dichlorophenyl)-
5-ethenyl-5-methyl-2,4-oxazo-
lidinedione and its metabolites
containing the 3,5 dichloro-
Residue: _____

Residue (if Step 9): _____

Analysis in crop(s)

Crop(s) Limit (mg/kg)

Crop(s) Tol. (ppm)

<u>Onions, green and</u>	
<u>dry bulb</u>	<u>1.0</u>
<u>Settuce</u>	<u>10.0</u>
<u>Raspberries</u>	<u>10.0</u>

CANADIAN LIMIT

Residue: _____

MEXICAN TOLERANCIA

Residue: _____

Crop Limit (ppm)

none

Crop Tolerancia (ppm)

none

Notes: