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PP# 8F2067. DaconilTM (chlorothalonil) on plantains and bananas.
Evaluation of analytical methods & residue data.

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PM #21 and TOX

Thru: Chief, Chemistry Branch

Diamond Shamrock Corporation proposes that the following tolerances be established for residues of chlorothalonil and its 4-hydroxy metabolite on bananas and plantains:

0.5 ppm on the whole fruit of which no more than 0.05 ppm shall be in the edible pulp.

The proposed use is limited to the Republic of Honduras.

Tolerances for combined residues of chlorothalonil and its 4-hydroxy metabolite have been (or are in the process of being) established on a number of r.a.c.'s ranging from 0.1 ppm in potatoes to 15 ppm in or on several vegetables. There are two other pending tolerance proposals.

Conclusions

1. The fate of Daconil in or on plants has been adequately described. The terminal residue consists of the parent compound and its 4-hydroxy metabolite. Technical Daconil contains no more than [redacted] hexachlorobenzene (HCB). Data presented in PP# 4E1502 demonstrate that no significant residues (* or <0.01 ppm) of HCB are likely to occur on treated crops.
2. Adequate analytical methods are available for enforcing the proposed tolerance.
3. Residues on treated bananas and plantains and in the edible pulp derived therefrom will not exceed the proposed tolerances for bananas, plantains and their edible pulps when used as described.
4. Neither of the r.a.c.'s involved in the petition are feed items; thus, the established and proposed uses of Daconil fall into Category 3 of Section 180.6(a).

*Note: The correct CA name for chlorothalonil does not include the numerical (2,4,5,6-) prefix and it is the one used in 40 CFR, §180.275.

PRODUCT IMPURITY INFO IS NOT INCLUDED

Recommendations

We recommend that the proposed tolerances for bananas and plantains grown in Honduras be established. We believe the tolerance, if established, should not bear any reference to Honduras since bananas as marketed here will have no natural identity.

Detailed Considerations

Formulation

The formulations proposed are Diamond Shamrock Corporation's Bravo^(R) 6F and Daconil 2787 W-75. Bravo^(R) 6F contains 5.0 lb of chlorothalonil/gal. Daconil 2787 W-75 is the foreign trade name for Bravo W-75 (See PP# 2F1230). Technical chlorothalonil is 95.6-98.6% pure; impurities in the product include [REDACTED]

[REDACTED] A description of the manufacturing process was submitted in connection with PP# 4E1502 and was discussed in our review of that petition (memo of 11/27/74, R. Schmitt).

The possibility of HCB in the technical chlorothalonil was discussed in connection with PP# 4E1502 and we concur with the conclusion reached in that case (memo of 11/27/74, R. Schmitt), that no HCB residue problem exists from the use of chlorothalonil. However, Daconil does contain up to [REDACTED] HCB.

Proposed Use

Uses

For use on bananas and plantains, Daconil is applied as follows:

Bananas- For use in bananas grown in Honduras* only: Apply 0.75 to 1.5 pints of Bravo 6F or 1 to 2 lbs of Daconil 2787 WP (i.e., 0.75 to 1.5 lbs. act/A) in to 2 to 5 gallons of water per acre. Applications are to be made by aerial application only to control black Sigatota leafspot disease. Applications are to be repeated every 10 to 14 days. There is no prescribed PHI.

Nature of the Residue

No new metabolism studies were submitted with this petition.

*Although not specifically so stated on the label, Eugene Wilson, Ph.D., PM No. 21, informed the writer that the petitioner's intent is to sell the fungicide in Honduras only (where the disease is localized in the Western hemisphere) and that the FR Notice establishing the tolerance will indicate that the tolerances are for bananas and plantains grown in Honduras only. See Also Other Considerations (below).

PRODUCT IMPURITY INFO IS NOT INCLUDED

The metabolism of chlorothalonil in plants and animals has been reviewed most recently in conjunction with PP# 661871 (memo of 1/11/77, M. J. Nelson). Studies submitted previously on plants (corn, tomatoes, potatoes) and animals (dogs, rats, cows), indicate that the residue of concern in both plants and animals consists of the parent and 4-hydroxy-2,5,6-trichloroisophthalonitrile. The 4-hydroxy metabolite comprises at most 10% of the residue in plants. The residue in plants is mainly surface in nature and the pesticide is not translocated in the aerial plant parts. Residues occurring in root crops probably result from run-off into the soil. The major residue of concern in animals, although it comprises only a minor % of the residue in plants, is the 4-hydroxy metabolite due to its propensity for transferring to meat and milk.

We conclude that the nature of the residue in bananas and plantains is adequately understood from data on other crops. The terminal residue of concern consists of the parent and the 4-hydroxy metabolite. On bananas and plantains, these would be surface residues on fruit which are unbagged early in the fruit development stage. According to information received from Mr. David Baldwin, Chiquita Banana Co. (United Brands Corp), Montvale, N. J., all bananas grown in Honduras (as well as in major exporting countries) are bagged as soon as the immature fruit are formed. There would be occasions when isolated stalks would not be bagged or have torn bags, but these would be relatively rare occurrences. Plantains are a minor export item, not grown on plantations and not bagged, according to Mr. Baldwin.

Analytical Method

The current method of enforcement for chlorothalonil tolerances is described in PAM II and involves extraction of both the parent and the 4-hydroxy metabolite with acidified acetone, separation of the two components on a Florisil column, conversion of the 4-hydroxy metabolite to its methyl ether and determination of both the parent and the derivatized metabolite via glc in separate analyses. This method has undergone a successful method trial for both the parent and the 4-hydroxy metabolite on peanuts fortified at 0.3 and 0.6 ppm and on broccoli fortified at 2.5 and 5.0 ppm.

In the Philippine study, whole bananas, were stripped with acetone using 500 mls per 2-3 whole bananas, by tumbling in a sealed jar (see below for remainder of procedure). The samples of the pulp of bananas were blended with acidified acetone (as for other crops) for one minute; tumbled for 2 hours in a sealed jar and filtered under vacuum.

Aliquots from the stripped bananas or the extracted pulp were evaporated to dryness and the residues taken up in dilute aqueous NaHCO_3 , the pH adjusted to 4.5 and the chlorothalonil residues extracted with isopropyl ether. The 4-hydroxy metabolite residues were then isolated by lowering the pH to 2.0 and extracting the metabolite with isopropyl ether.

After evaporation of the ether extracts, Daconil and its metabolite were separately determined by ECGC, after the metabolite was converted *with* the use of 1-n-propyl-3-p-tolyltriazene vs. the methylating agent used in PAM II). It should be noted that the banana methods also include column chromatographic cleanup of Daconil and its 4-hydroxy metabolites (as in the PAM II method).

Recovery data for whole bananas indicates that, at fortification levels of 0.02 and 0.07 ppm for Daconil and of 0.05 to 0.07 ppm for the metabolite, recoveries ranged from 83-110% (ave = 93%) for Daconil and from 70-93% (ave = 84%) for the metabolite.

In the edible pulp, corresponding recoveries were 58-80% (avg was ca. 73%) for Daconil (in the range of 0.04 to 0.1 ppm) and 58-69% (avg. was ca. 64%) for the metabolite.

In analyses of the pulp of and whole bananas in the Honduras study, interference in the GLC determination of chlorothalonil per se was detected. This interference was eliminated by using an alumina column with methylene chloride as the eluting solvent (see Addendum 1, pp. D 57 - D 58 of the petition). Recoveries by this procedure ranged from 65-80% for parent compound (at the same levels). These data for the whole bananas from Honduras were generated by a procedure which involved the maceration of the whole bananas instead of stripping. The determinative steps are the same as those used in PAM II.

Overall, we find the method as modified for the Honduras bananas to be adequate for enforcement.

Note: The method for bananas and its pulp (as modified in the Honduras study) should be added to PAM II, since it differs significantly from the PAM II method. We do not consider a method trial necessary as the proposed use results in a "no-residue" situation for the edible part of bananas and plantains. In addition, the variations in the extraction and isolation procedures used for residues on bananas are based on well understood and accepted techniques and the determinative steps are essentially the same as those in the PAM II method.

Residue Data

The number of studies is quite limited. However, considering that chlorothalonil is a surface residue, plus the fact that there is little likelihood of any real residues in the edible parts of imported bananas (which must be washed and treated with fungicides prior to shipment), we are not questioning the adequacy of the data. However, for any future proposal which involves an expansion of the use to a country other than Honduras, we may require additional residue data for such a proposal.

Also, it should be noted that there are no data for plantains per se. However, bananas and plantains are essentially botanically equivalent and are considered to be equivalent as provided for in Section 180.1(h), CFR 40 (see also Reed memo in Petition Review Aids). Thus, by translation, the data for bananas are adequate for the purposes of the proposed tolerance for plantains and their edible pulp. *See pp. B 3 and B 6, PP# 8F0674.

The available studies are two from the Philippines and one from Honduras. However, two of the three studies included data for both bagged and unbagged bananas as well as for unwashed bananas (whether bagged or not). Aerial applications (as provided for by the label) were involved in all studies. Due to the various factors discussed above, we are translating the data from the Philippines studies to the proposed use in Honduras.

In the Philippines studies, the maximum residue on whole unwashed, unbagged bananas was 0.06 ppm (by stripping) and 0.11 ppm (by maceration) on samples taken immediately after last application. For the bagged bananas, whether washed or unwashed, residues of Daconil per se were no more than 0.02 ppm and the metabolite was never detected in any sample. In the edible pulp (after removal of peel), Daconil and its metabolite were never detected in any sample.

1.16 to
1.3 lb
a.i./A

In the single Honduras test, 12 applications made within 103 days (for a total of 18 lbs. active/A) were applied. On the day of the last application, samples of bagged and unbagged fruit were taken for analyses. The maximum residue on any sample of unwashed, unbagged whole fruit was <0.2 ppm whereas there were maximum residues of 0.02 ppm on the bagged fruit (whether washed or unwashed). After washing, the maximum residue on the unbagged whole fruit was 0.05 ppm (average = 0.02 ppm) of Daconil per se. Residues of the metabolite were non-detectable (i.e., <0.01 ppm). Residues of parent and metabolite were undetectable (<0.01 ppm) in the edible pulp, whether from bagged, unbagged, washed or unwashed bananas.

1.3 lb
a.i./A

Consequently, we find the proposed tolerance of 0.5 ppm for bananas and plantains (whole fruit) to be adequate---also that, for the edible pulps, combined residues will not exceed the proposed tolerance of 0.05 ppm. The data suggest that the proposed tolerance level of 0.5 ppm may be somewhat higher than necessary. However, due to the limited amount of residue data, we find it to be acceptable.

Residues in meat, milk, poultry and eggs

There are no feed items for livestock or poultry involved in the proposed tolerances. Therefore, the proposed uses as well as the existing uses, are placed in category 3 of 180.6(a).

Other Considerations

The petition involves uses in a foreign country and there will be no registered uses for bananas or plantains in the United States.

It is our policy to require some information as to the regulating practices in foreign countries when United States tolerances are requested for uses in those countries.

The petition for bananas and plantains contains a letter from the Minister of National Resources of the Republic of Honduras which approves the use pattern submitted in this petition. Previous information supplied to us in connection with PP# 6E1670 indicated that there is no registration requirement for pesticide use in Honduras. If this tolerance is established, we would probably have to rely on the large fruit companies to exert control over the use of this product. The three banana exporters in the Honduras are: United Fruit Co., Standard Fruit Co., and Castle-Cook Co. (Dole Brand) (information received by telecon on 4/12/78 by W. S. Cox from J. R. Lucietta, Diamond Shamrock Corp.).

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