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OFFICE OF
PESTICIDE AND TOXIC SUBSTANCES

PP#1G2428. Chlorothalonil on citrus. Amendment of 9/24/81.

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This amendment is in response to our memorandum of 3/10/81 detailing deficiencies in the original submission. The reasons for rejection, the petitioner's response and our comments are listed below.

1. Data on the level of pentachlorobenzonitrile (PCBN) in technical chlorothalonil should be submitted.

Response:

A complete composition of technical chlorothalonil (confidential) as submitted February 25, 1976 with the cover letter to PP#6F1749. I included a maximum amount of 2.5% Pentachlorobenzonitrile (PCBN) in technical chlorothalonil. Bravo 500 would therefore contain no more than 1.03% PCBN maximum.

Comment:

We consider this deficiency resolved.

2. We are unable to conclude that residues of the impurities hexachlorobenzene (HCB) and PCBN will not present a residue problem. Residue data are needed.

Response:

MANUFACTURING PROCESS INFORMATION IS NOT INCLUDED

The Bravo 500 used in the present method validation study assayed 40.6% chlorothalonil, [REDACTED]. The following table shows mean residue levels of chlorothalonil, PCBN, and HCB on oranges harvested immediately following the last of three applications of the Bravo 500 at 11 pints per acre as determined by both use of surface extraction of whole oranges and the use of maceration extraction and the calculated values of PCBN and HCB for the same samples.

	determined		calculated	
	surface	maceration	surface	maceration (in ppm)
chlorothalonil	11.22	10.07	--	--
PCBN	0.098	0.068	0.091	0.082
HCB	0.006	0.004	0.0058	0.0052

In addition to showing that the chlorothalonil, PCBN, or HCB residue data obtained by either the surface extraction or by the maceration extraction are valid, the data also show the residue of PCBN and HCB are proportional to the level of chlorothalonil residues.

The following table shows the mean residues as above ~~except~~ the studies were conducted at 14 and 28 days after the last application i.e. weathered residues.

	determined		calculated	
	surface	maceration	surface	maceration (in ppm)
chlorothalonil	5.27	4.10		
PCBN	0.043	0.038	0.043	0.033
HCB	0.003	<0.003	0.0027	0.0021

These data show that both the surface extraction and the maceration extraction procedure are valid for the extraction of weathered residues of chlorothalonil, HCB and PCBN. The data also show the level of HCB and PCBN residues are directly proportional to the level of chlorothalonil residue.

It should be pointed out that Section B has been revised to state "DO NOT apply when previous season's fruit is on the tree". For purposes of validating the analytical method, the present study was run on mature fruit; however, when used according to proposed directions for use, applications will be made to immature fruit with resulting chlorothalonil residues in the raw agricultural commodity expected to be less than 0.1 ppm.

Because weathered residues of HCB and PCBN have been shown to be in the same proportion to weathered residues of chlorothalonil as proportions known to exist in the formulation, it is evident that if weathered residues of chlorothalonil will not exceed 0.1 ppm there will be no detectable residues of HCB or PCBN at levels of method sensitivity.

Comment:

This validation study alleviates our concern about the residues from HCB and PCBN presenting a problem. No further residue data are needed.

We consider this deficiency resolved.

3. The proposed 100 day PHI is not practical, as certain varieties of citrus have nearly mature fruit on the tree at the suggested time of application. You should propose a specific PHI less than 20 days (as indicated elsewhere in the petition) or else restrict the use to early maturing varieties from which fruit is completely harvested prior to blooming.

Response:

This question was discussed in length at our April 7, 1981 meeting and resolved. The proposed label has subsequently been changed to read, "DO NOT apply when previous season's fruit is on the tree".

Comment:

While this restriction would resolve our concern about citrus which are not harvested before the next season's fruit appears, it results in there being in effect no PHI for citrus that only produce one major flush. The restriction should be reworded as follows: "DO NOT apply within 100 days of harvest or the when previous season's fruit is on the tree."

We do not consider this deficiency resolved.

4. Section B should state a maximum number of applications which will be made. The accompanying EUP indicates that up to 5 applications will be made, whereas Section B indicates possibly only two. Section B should be revised to reflect the use intended for the experimental program.

Response:

It is unclear why EPA concluded that possibly only two applications may be indicated in Section B. The revised labeling gives explicit directions for use on each of the diseases claimed. Timing and directions clearly state that a maximum of five (5) applications can be made. To further clarify this we have proposed adding the statement to the label, "DO NOT apply to citrus more than five times per season". The timing and number of applications are in agreement with the proposed field program (Section G).

Comment:

We consider this deficiency resolved.

5. The EUP indicates that all varieties of citrus will be treated, while Section B gives only the proposed use for oranges and grapefruit. Section B should accurately reflect the proposed experimental program.

Response:

Section B has been corrected to give directions for use on all varieties of citrus.

Comment:

We consider this deficiency resolved.

6. If the proposed use is indeed only for oranges and grapefruit, Section F should be so worded. Resubmit a new Section F which reflects the proposed EUP labeling.

Response:

See response to question Number 5 above. Since the proposed use is for "citrus" there is no need to revise Section F, therefore, proposed tolerances of 0.1 ppm on the raw agricultural product citrus and 10 ppm food additive tolerance on citrus oil shall remain as requested.

Comment:

We consider this deficiency resolved.

7. Adequate analytical methodology is not available to detect residues of parent chlorothalonil in citrus. You should run a comparison study for surface extraction vs maceration using citrus samples bearing significant levels (1 ppm or more) of weathered residues. If the surface extraction method proves less efficient, a validated method employing maceration of whole fruit will be required.

Response:

See enclosed report and the response to No. 2. It is concluded that the surface extraction method and maceration of whole fruits are equally valid methods for determining residues of chlorothalonil in citrus. The submitted validation study (Document No. 506-3CR-81-0182-001) is strictly a validation study and should not be used for establishing use patterns.

Comment:

The validation study discussed in the response to Deficiency 2 is adequate to show that both surface extraction and maceration of whole fruits are valid methods.

We consider this deficiency resolved.

8. Analytical methodology for determining residues of 4-hydroxy-2,5,6-trichloroisophthalonitrile in whole citrus fruit should be submitted, along with appropriate validation data. The methodology should employ maceration of the fruit.

Response:

All previously submitted data for residues of the metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile were obtained by an analytical procedure employing maceration extraction. The method, validation and explanation as to why maceration is preferred are submitted as part of the enclosed report.

Comment:

The validation study shows that the previously submitted data are valid.

We consider this deficiency resolved.

9. Until the requested method comparison study is available we are unable to conclude that the residue data submitted are valid.

Response:

In the comparison study, residue data were obtained by use of both surface extraction and maceration procedures. In this study it was demonstrated that either extraction procedure was valid for determining residues of chlorothalonil, HCB and PCBN, therefore, studies submitted with the petition are considered valid.

Comment:

We consider this deficiency resolved.

10. The proposed 0.1 ppm temporary tolerance for citrus is not adequate. In order to determine the appropriate tolerance level, residue data reflecting the maximum number of applications at the maximum proposed rate and a more practical PHI including some data for the 4-hydroxy metabolite will be required.

Response:

By prohibiting the use of Bravo when the previous season's crop is still on the tree and by validating the analytical method, the 0.1 ppm temporary tolerance for citrus should be acceptable. Residue data on the 4-hydroxy metabolite are submitted in the validation study.

Comment:

Data were not submitted reflecting the maximum number of applications at the maximum proposed rate. Additionally, no PHI has been established for citrus which may be harvested before new fruit appears (see 3 above).

However, data are available which show no detectable residues on lemons following two applications at 2.7 x the maximum proposed rate and a 110 day PHI. Since the additional three applications will be made 1-4 months prior to these, we conclude that residues of chlorothalonil on citrus will not exceed 0.1 ppm provided the label restriction is reworded to include a 100 day PHI for fruit not presently covered by a PHI.

For a permanent tolerance, additional residue data reflecting the proposed 5 applications will be required.

We consider this deficiency resolved.

11. Residue data for HCB and PCBN using an acceptable analytical method and fruit containing significant levels of chlorothalonil residues should be submitted.

Response:

Refer to response to No. 2 above concerning assayed residue levels for HCB and PCBN versus calculated levels based on chlorothalonil residues and proportional concentrations of HCB and PCBN in the Bravo 500.

Comment:

We consider this deficiency resolved.

12. We are unable to draw a final conclusion regarding the adequacy of the proposed 10 ppm food additive tolerance for citrus oil until such time as an appropriate level for oranges and grapefruit is decided on. The available processing study is considered adequate.

Response:

Validation of the residue methods used should enable the EPA to accept the data previously submitted as valid and representative. The proposed 0.1 ppm tolerance on the raw agricultural commodity is adequate for the proposed use. A concentration factor in oil of 100X means that 10 ppm in citrus oil is adequate.

Comment:

Provided the label restriction is amended to include a 100 day PHI for citrus not presently covered by a PHI, we would consider a 10 ppm food additive tolerance for citrus oil to be appropriate.

We consider this deficiency resolved.

13. We are unable to draw any conclusions regarding secondary residues in meat and milk until appropriate tolerance levels are determined for oranges and grapefruit and we can determine whether residues will be present in citrus pulp. If residues are present in dried citrus pulp, we tentatively conclude that secondary residues will occur in meat and milk.

Response:

Because use directions prohibit applications when the previous season's

fruit (mature fruit) is still on the tree, all applications will be made to immature fruit. Residue studies previously submitted are representative of maximum residues expected when used according to proposed directions. Based upon those studies, including a processing study found to be acceptable, EPA should conclude that residues will not be a concern in citrus pulp and will not reasonably be expected to occur in meat and milk.

Comment:

If the label restriction were reworded to include a 100 day PHI for citrus not presently covered by a PHI, we would not expect detectable residues of chlorothalonil and its hydroxy metabolite in dried citrus pulp. Therefore, this use would fall into Category 3 of §180.6(a) with respect to secondary residues in meat and milk.

We consider this deficiency resolved.

Conclusions.

1. Residues of the impurities hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN) will not present a residue problem.
2. The proposed restriction against applying chlorothalonil when the previous season's fruit is on the tree is not adequate to reflect all uses. An adequate wording would be: "DO NOT apply within 100 days of harvest or when the previous season's fruit is on the tree."
- 3a. Adequate methodology is available for determining residues of parent chlorothalonil in citrus.
- 3b. Adequate methodology is available for determining residues of the metabolite 4-hydroxy-2,5,6-trichloroisophalonitrile in citrus.
- 4a. The proposed 0.1 ppm temporary tolerance for citrus is adequate for the purpose of this request, provided that Section B is revised as indicated in Conclusion 2.
- 4b. The proposed 10 ppm food additive tolerance for citrus oil is adequate provided that Section B is revised as indicated in Conclusion 2.
5. We conclude that secondary residues will not occur in meat and milk from the proposed use provided that Section B is revised as indicated in Conclusion 2.

Recommendations

For the reason cited in Conclusion 2, we recommend against the establishment of these temporary tolerances. We would have no objection if the label restriction were revised to read "Do not apply within 100 days of harvest or when the previous season's fruit is on the tree."

For a permanent tolerance, we will require residue data reflecting the proposed 5 applications.