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

DIAMOND SHAMROCK CORPORATION
Agricultural Chemicals Division
Attn: J. R. Lucietta
1100 Superior Avenue
Cleveland, OH 44114

Dear Mr. Lucietta:

This letter refers to Pesticide Petition 6F1749 proposing establishment of tolerances for the combined residues of the fungicide Chlorothalonil (tetrachloroisophthalonitrile) and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile in or on the raw agricultural commodities peaches at 25 parts per million (ppm), cherries (tart and sweet) at 15 ppm, and your application for amended registration dated February 25, 1976, for Bravo 6F(EPA Registration No. 677-313).

We have completed our review of this petition and find that we cannot act favorably on it. For further consideration of the proposed tolerances, the following should be submitted:

1. Submit an amended Section F. increasing the proposed tolerance for cherries to 25 ppm. Residues from the proposed use on cherries may exceed the proposed tolerance of 15 ppm. A tolerance of 25 ppm for cherries will be needed to cover such residues.

2. The data for fruit (peaches and cherries) grown in the Mountain and West Coast States are too meager to allow us to make any conclusions as to an adequate tolerance level for the proposed uses in these areas. Consequently, the label must be amended to prohibit the use of chlorothalonil in the Mountain and West Coast States except when used for control of peach leaf curl (dormant application only). Submit an amended Section B (label) reflecting the following restrictions:

(A) "Do not allow livestock to graze treated areas".

(B) "Do not use on cherries (or peaches) grown in either the Mountain States or the West Coast States" (except for use on peaches to control peach leaf curl). Alternatively, adequate residue data for peaches and cherries grown in those states should be submitted to support the proposed post-petal fall uses.

3. The claims for use to control diseases on sweet cherries are not adequately supported by the data. Brown rot was not controlled in either of the two tests on sweet cherries and cherry leaf spot data were included in only one of these tests. Delete sweet cherries from the label.

4. The data did not adequately demonstrate control of Rhizopus rot on peaches and no tests were conducted for Rhizopus rot control on cherries. Delete claims for Rhizopus rot control on both crops.

5. The following environmental chemistry data requirement, as given in Section 3 of the regulations has not been addressed: Effect of pesticides on microorganisms. To assess the impact of pesticides on soil microbes the following are needed:

(a) Population analyses using a variety of selective procedures including the use of restrictive growth media, the use of special isolation techniques (i.e. Anaerobic isolation, thermophilic) isolation) and direct counting procedures are to be made to determine the effect of the chemical on normal soil microflora.

(b) Effects on the enzyme activity of mocrobes that degrade the pesticide should be determined. Additionally, effects on general soil enzyme activities such as soil dehydrogenase and phosphatase may be determined.

(c) Change in population of common pesticide degraders such as Bacillus sp., actionomycetes, pseudomonads, coryneform bacteria, Trichoderma, Aspergillus, etc. should be determined.

(d) The effects on the transformations of nitrogen compounds should be determined.

(e) Effects on carbohydrate transformations should be determined.

6. In addition, the following submitted studies are insufficient to assess the environmental chemistry hazard.

(a) Photodegradation of Daconil in aqueous solutions. Submit an explanation for the reactivity of Daconil in buffered solution suggested by this study, and the stability of Daconil in the identical buffers in the hydrolysis study.

(b) Degradation of Daconil and its Metabolite, 4-hydroxy 2,5,6-trichloroisophthalonitrile, in soil: in order to determine the rate of pesticide degradation, more than two data points are needed. Soil should be aged at 25 degrees C. Data should be sufficient to estimate the half life of total C-14 and its composition in soil.

(c) Aerobic and Anaerobic Soil Metabolism of Daconil: aerobic soil metabolism requires the use of an apparatus that can monitor volatilization products; however, the apparatus used must allow sufficient airflow so that the atmosphere doesn't become saturated with CO-2. It is preferable that soil samples be aged in containers larger than test tubes.

(d) Bound Residue Study - Appendix I: soils should not be extracted with .3N HCl prior to removal of the extractable residues (i.e. acidified acetone wash). This is not the procedure used elsewhere in this report.

(e) At this time the microbial study submitted will constitute an acceptable aerobic soil study for the proposed use.

(f) Based on the studies submitted, we assume DAC-3701 is stable in soil. Therefore, rotational crop studies may be required for other use patterns.

(g) An anaerobic soil metabolism study, using soil aged at 25 degrees C, may be required for other use patterns.

Requirements For Registration Renewal.

I. Based upon proposed use patterns, persistance and leaching capabilities of the major matabolite, the acute toxicity to fish and the magnitude of bioconcentration in fish, both chronic fish and avian studies for Daconil will be required prior to consideration for registration renewal.

II. In addition, special tests using the major degradation product (DAC-3701) will also be required. These special tests will include:

(A) A 96-hour LC-50 for 1 species of warm water fish.

(B) A 48-hour LC-50 for an aquatic invertebrate.

(C) An acute oral LD-50 for 1 species of waterfowl or 1 species of upland game bird.

Additional studies may be required pending results of these tests.

We suggest you contact the environmental safety staff to discuss protocol for the studies mentioned in items I & II.

Sincerely,

Eugene M. Wilson

Eugene M. Wilson
Product Manager (21)
Fungicide-Herbicide Branch
Registration Division (WH-567)

APPENDIX

Response to a letter from the Environmental Protection Agency regarding PP 6F1749 dated August 3, 1976

1. Submit an amended Section F, increasing the proposed tolerance for cherries to 25 ppm. Residues from the proposed use on cherries may exceed the proposed tolerance of 15 ppm. A tolerance of 25 ppm for cherries will be needed to cover such residues.

   Response: Section F is amended and the proposed tolerance for cherries is 25 ppm.

2. The data for fruit (peaches and cherries) grown in the Mountain and West Coast States are too meager to allow us to make any conclusions as to an adequate tolerance level for the proposed uses in these areas. Consequently, the label must be amended to prohibit the use of chlorothalonil in the Mountain and West Coast States except when used for control of peach leaf curl (dormant application only). Submit an amended Section B (label) reflecting the following restrictions:

   (A) "Do not allow livestock to graze treated areas."

   (B) "Do not use on cherries (or peaches) grown in either the Mountain States or the West Coast States" (except for use on peaches to control peach leaf curl). Alternatively, adequate residue data for peaches and cherries grown in those states should be submitted to support the proposed post-petal fall uses.

   Response: Section D is amended with additional residue data for peaches and cherries grown in the Mountain and West Coast States. The restriction "DO NOT allow livestock to graze treated areas" is incorporated in the revised label, Section B (Amended).

3. The claims for use to control diseases on sweet cherries are not adequatel supported by the data. Brown rot was not controlled in either of the two tests on sweet cherries and cherry leaf spot data were included in only one of these tests. Delete sweet cherries from the label.

   Response: The claim to control diseases on sweet cherries has been deleted from the label.

4. The data did not adequately demonstrate control of Rhizopus rot on peaches and no tests were conducted for Rhizopus rot control on cherries. Delete claims for Rhizopus rot control on both crops.

   Response: The claim for Rhizopus rot has been deleted from the label.

5. The following environmental chemistry data requirement, as given in Section 3 of the regulations has not been addressed: Effect of pesticides on microorganisms.

To assess the impact of Daconil on microorganisms the following studies are included as an amendment to Section J, Environmental Chemistry:

(a) Effect of Chlorothalonil on populations of soil microorganisms.

(b) The Effect of Chlorothalonil on soil microflora.

(c) Effect of Chlorothalonil on Soybean Nitrogen Fixation.

(d) Biodegradation of Daconil 2787
(Ref. Section D PP 1F1024 Page 91-96)

6. In addition, the following submitted studies are insufficient to assess the environmental chemistry hazard.

(a) Photodegradation of Daconil in aqueous solutions. Submit an explanation for the reactivity of Daconil in buffered solution suggested by this study, and the stability of Daconil in the identical buffers in the hydrolysis study.

It has been previously proven that the reactive site of the Daconil molecule is the halogen in the fourth position on the benzene ring. The reactivity of this halogen is enchanced by photoirradiation as demonstrated in the photodegradation studies conducted on silica gel plates. Under conditions employed in this study, Daconil degraded to give 4-hydroxy 2,5,6-trichloroisophthaloritrile as well as its metallic salts.

In the hydrolysis study, Daconil was stable when exposed to phosphate buffered solutions at pH 5 and 7 in the absence of light. However, upon exposure of Daconil in phosphate buffered solutions to artificial sunlight, 90% of the parent material was converted to polar water soluble products which could not be partitioned into organic solvents. It was postulated that the product was a phosphate salt of Daconil. Presumably the intensity of the irradiation was sufficient to activate the fourth position

of the Daconil ring. In the same study it was shown that in the presence of 0.1N HCl, no photohydrolysis of Daconil occurred.

(b) **Degradation of** Daconil and its Metabolite, 4-hydroxy 2,5,6-trichloroisophthalonitrile, in soil: in order to determine the rate of pesticide degradation, more than two data points are needed. Soil should be aged at 25 degrees C. Data should be sufficient to estimate the half life of total C-14 and its composition in soil.

The half-life of Daconil in soil was determined under controlled environmental conditions. The report titled "Effect of Microorganisms Upon The Soil Metabolism of Daconil and 4-hydroxy 2,5,6-trichloroisophthalonitrile" was submitted in Section J, Page 208, of Pesticide Petition 6F1749.

In this study, temperature was maintained at 25 degrees C, seven data points were obtained over the 90 day test period. Since the decline of chlorothalonil was shown to follow first order kinetics (reference J213) the half-life of Daconil was calculated according to the equation cited on J213 using data obtained at T=22 days.

The purpose of the report sited "Degradation of Daconil and It's Metabolite, 4-hydroxy 2,5,6-trichloroisophthalonitrile in Soil", was to obtain quantities of "aged" soil fortified with Daconil for subsequent studies such as leaching of soil degradation products. The data combined in the sited report was not used to determine the half-life of Daconil in soil.

(c) Aerobic and Anaerobic Soil Metabolism of Daconil: aerobic soil metabolism requires the use of an apparatus that can monitor volatilization products; however, the apparatus used must allow sufficient airflow so that the atmosphere doesn't become saturated with CO-2. It is preferable that soil samples be aged in containers larger than test tubes.

In the study to determine the effect of soil microorganisms on the metabolism of Daconil, five soil types were amended with ^{14}C labeled Daconil. Analyses of these soils using the total

combustion technique were conducted immediately after fortification and again after 30 days storage under greenhouse conditions. (See Section J Pesticide Petition 6F1749, Page 121 and 142.) Since the results showed no loss of radioactivity, it was concluded that formation of $^{14}CO_2$ was not a significant factor in metabolism of ^{14}C labeled Daconil by soil microorganisms. Therefore, monitoring for $^{14}CO_2$ in the aerobic soil metabolism study was not considered necessary.

(d) Bound Residue Study - Appendix I: soils should not be extracted with .3N HCl prior to removal of the extractable residues (i.e. acidified acetone wash). This is not the procedure used elsewhere in this report.

In the Soil Bound Residue Study the soil samples were extracted by first acidifying with 12 ml of 0.3N HCl, mixing for five minutes before adding 50 ml of acetone. The resulting acid: acetone mixture was the extracting solvent. While this differs from the single addition of an 80:20 mixture of acetone: 0.3N HCl the end result should be essentially the same. We did not make two separate extractions, one with 0.3N HCl and the other with acetone, as implied in 6(c).

(e) At this time the microbial study submitted will constitute an acceptable aerobic soil study for the proposed use.

(f) Based on the studies submitted, we assume DAC-3701 is stable in soil. Therefore, rotational crop studies may be required for other use patterns.

Rotational crop studies will be conducted and submitted in support of future proposed use patterns for Daconil.

(g) An anaerobic soil metabolism study, using soil aged 25 degrees C, may be required for other use patterns.

The soil used for the anaerobic soil metabolism study was "aged" for 30 days under greenhouse conditions. The temperature in the greenhouse was maintained between 26 degrees C during the 14 hour light cycle and 20 degrees C during the 10 hour dark cycle. This temperature cycle is more consistent with natural environmental soil temperatures than the suggested 25 degrees C.