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

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP #2E2744: Chlorothalonil in Cocoa Beans and Coffee Beans. Evaluation of residue data and analytical method.

TO: H. M. Jacoby (PM-21)
Registration Division (TS-767)

FROM: Alfred Smith, Chemist
Residue Chemistry Branch, HED (TS-769)

THRU: Charles L. Trichilo, Chief
Residue Chemistry Branch, HED (TS-769)

The Diamond Shamrock Corporation proposes tolerances for residues of the fungicide chlorothalonil, (2,4,5,6-tetrachloroisophthalonitrile), and its metabolite (4-hydroxy-2,5,6-trichloroisophthalonitrile) at 0.05 ppm in or on cocoa beans and coffee beans.

Tolerances are established for chlorothalonil on a variety of commodities at levels of 0.10-15 ppm (§180.275). There are several other pending tolerance proposals.

Conclusions

1. The nature of the residue is adequately understood. The parent compound, chlorothalonil and its hydroxy metabolite are the significant components of plant residues. The manufacturing impurity HCB could be a part of the residue [see 3(c) below].

2. An adequate analytical method is available for enforcement purposes for chlorothalonil and its hydroxy metabolite.

3(a). Residues of chlorothalonil and its metabolites in cocoa beans are not likely to exceed the proposed tolerance in the countries for which data are submitted. Further, no residues of the formulation's impurities hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN) are noted in cocoa beans. A final conclusion on residues levels expected will be made when the question raised in conclusion 5 is resolved.

3(b). Residue of chlorothalonil and its metabolite in or on coffee beans could exceed the proposed tolerance (0.05 ppm). A level of 0.2 ppm is adequate to cover residues likely to cocur in the countries for which data are submitted. A final conclusion on residue levels expected will be made when the question raised in conclusion 5 is resolved.

3(c). Residues of HCB could occur in coffee beans at levels of approximately 0.01 ppm. We defer to TOX on the toxicological significance, if any, of HCB residues at this level. (No residues of PCBN were noted.)

3(d). Residues, if any, in the cocoa bean byproducts or the coffee bean byproducts (roasted coffee bean, powdered coffee, ground coffee) would be much less than the levels in the raw agricultural commodities (RAC).

4. Because no feed items are involved in this petition, there will be no problem of residues in meat, milk, poultry and eggs.

5. The countries in which the uses are intended for both coffee and cocoa plants should be submitted. This information is needed in order to fully evaluate the proposed uses.

6. There are no Codex, Canadian or Mexican tolerances for chlorothalonil on these commodities.

Recommendation

We recommend against the proposed tolerances. A favorable recommendation is contingent upon resolution of the questions raised in Conclusions 3(a), 3(b), 3(c), and 5.

Detailed Considerations

Proposed Use

Chlorothalonil, formulated as BRAVO® 500 containing 4.17 lbs. a.i. per gallon, is to be used as a foliar spray on cocoa bean and coffee bean plants.

The statement that the directions represent the pattern of use in important coffee growing areas outside the U.S. is too general. The countries in which the use is intended on both coffee and cocoa plants should be submitted. Such information is necessary in order to fully evaluate the proposed uses.

Cocoa beans

Apply 1.3 lb act/A. Begin at peak of flowering season and repeat at 7-14 day intervals. As pods mature and as rainfall decreases, increase to 14-21 day intervals.

Coffee beans

Apply 2.86 lbs act/A. Begin before onset of rainy season and continue at 21-28 day intervals.

Technical chlorothalonil

The manufacturing process for the technical grade chlorothalonil has been considered (cf. PP #6F1749). Technical chlorothalonil is 95.6-98.5% pure. Hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN) are the impurities of concern. The treated crops are examined for HCB and PCBN, and any residues found are fully evaluated.

The remaining impurities are not likely to produce a residue problem.

Nature of the Residue

The metabolism of chlorothalonil has been fully considered in previous petitions (cf. PP #6F1749). Studies with plants show that foliar deposits of chlorothalonil do not translocate, and there is no uptake from roots to aerial plant parts. The components of concern in plant residues are the parent compound, chlorothalonil, and its metabolite 4-hydroxy chlorothanil.

The nature of the residue is adequately understood.

Analytical Method

A sample is extracted by blending with an acidified acetone solvent and filtered. An aliquot of the filtrate is evaporated to dryness. The residue is taken up with a solution of sodium bicarbonate and adjusted to pH 4.5 with same. The residues of chlorothalonil, its metabolite, and the impurities HCB and PCBN are extracted into petroleum ether and the solvent is evaporated. (The aqueous phase is held for separate metabolite examination.)

The residue from the petroleum ether is taken up in a solution of hexane/methylene chloride, and an aliquot is air dried and held for cleanup and separation by florisil column chromatography.

Chlorothalonil is eluted from the florisil column with a solvent mix of methylene chloride/hexane/acetonitrile. A separate column is used for HCB and PCBN. HCB is cleaned up and eluted with a methylene chloride/hexane solution, and the PCBN is eluted with a solvent system of acetonitrile/hexane/methylene chloride. The separate eluates are evaporated, taken up with toluene, and determined by gas chromatography using an electron capture detection system (ECGC).

The sodium bicarbonate aqueous phase is adjusted to pH^2 and extracted with petroleum ether which is evaporated. The residue is treated with a methylating agent which converts the 4-hydroxy metabolite to the methyl ether. The solvent is evaporated, and the residue is taken up with acidified petroleum ether and determined by ECGC as above. (If needed, an alumina column is available for additional cleanup.)

The method for chlorothalonil and its 4-hydroxy metabolite is essentially the same as that in PAM II as method I. The method has been successfully tested by FDA on potatoes at levels of 0.1 ppm and 0.2 ppm and EPA on peanuts (0.3 ppm and 0.6 ppm) and broccoli at levels of 2.5 ppm and 5.0 ppm.

Untreated (control) samples of cocoa beans had no detectable residues of chlorothalonil (<0.03 ppm), 4-OH metabolite (<0.03 ppm), HCB (<0.004 ppm), and PCBN (<0.008 ppm). Control samples were fortified with chlorothalonil (0.1-10 ppm), 4-OH metabolite (0.05-0.50 ppm), HCB (0.01-0.05 ppm), and PCBN (0.02-0.10 ppm). Overall recoveries were 60-110%.

Control samples of coffee beans had no detectable residues of chlorothalonil (<0.01 ppm) -0.04 ppm, 4-OH metabolite (<0.01 ppm), HCB and PCBN (<0.005 ppm). Control samples were fortified with chlorothalonil (0.1-10 ppm), 4-OH metabolite (0.05-0.5 ppm), HCB (0.01-0.05 ppm), and PCBN (0.02-0.10 ppm). Overall recoveries were 60-127%.

The method is adequate for the determination of residues of chlorothalonil, its metabolite 4-OH-chlorothalonil, and the components HCB and PCBN.

An adequate analytical method is available for enforcement purposes.

Residue Data

Cocoa beans

Samples were obtained from crops grown in Brazil, Mexico, Ecuador, and Costa Rica. Applications were made to fruiting cocoa plants, and the bean samples were taken from mature pods. Crops were treated 4-11 times at rates of 0.8X-1.7X proposed rate. Harvest occurred at intervals of 14-60 days after the last treatment (PHI). Overall residues from all treatments were none detectable (ND, <0.03 ppm)-0.04 ppm.

Residues of HCB and PCBN were none detectable (<0.03 ppm and <0.008 ppm, respectively) from all treatments.

For harvest, the beans are removed from a large fruit or pod of the cocoa tree. The beans then undergo a fermentation process to remove the pulp surrounding each seed. The beans are then dried, sacked, and shipped.

The cocoa bean is not treated directly. We would expect residues, when present, on the bean to be due to incidental contamination since chlorothalonil is a contact fungicide and is not systemic.

The cocoa pod may be harvested on the day of treatment (0-day). The earliest interval from treatment to harvest is 14 days. However, because of the nature of propagation of the cocoa bean, it is reasonable to assume that the residue data adequately reflect the residue levels expected on the cocoa beans from the proposed use.

Cocoa Processing

The cocoa bean is roasted at 800-1000°F for approximately one-half hour. The shells are discarded, and the insides are ground at 300-400°F which produces cocoa butter and chocolate liquor which is processed further.

Due to the harsh processing conditions, residues on the bean will be considerably reduced. The grinding process will further reduce any residues present. Therefore, it is reasonable to conclude that residues, if any, in the cocoa bean byproducts will be less than the level in the bean.

Residues of chlorothalonil and its metabolite are not likely to exceed the proposed tolerance (0.05 ppm) from the proposed use. Additionally, no residues of the formulation's impurities HCB and PCBN are noted in cocoa beans.

Coffee

Samples were obtained from crops grown in Brazil which had received five applications at rates of 0.34X and 0.75X proposed rate. The berries were surface extracted, and the beans were removed. Each component was examined for residues of chlorothalonil and its 4-hydroxy metabolite.

The berries had residues of 3.26-3.51 ppm at 0.34X and 3.73-4.38 ppm at 0.75X when harvested on the day of the last treatment (0-day). The beans had trace residues of chlorothalonil of 0.08-0.10 ppm (0.34X) and 0.10-0.12 ppm (0.75X). No detectable residues of the 4-hydroxy metabolite (<0.01 ppm), HCB (<0.003 ppm) and PCBN (<0.005 ppm) were noted.

The foregoing study indicates that residues are confined mainly on the coffee berry with trace residues occurring on the coffee bean which is the item of commerce.

In a study of coffee grown in the Cameroon (Africa), the samples were collected from crops which had received five applications at rates of 0.8X and 1.1X and harvested 122 days after the last treatment. The beans were removed from the berries and analyzed for residues. Trace residues of chlorothalonil (ND-0.05 ppm) and the impurity HCB (0.005-0.011 ppm) were noted. No detectable residues of the 4-hydroxy metabolite (0.03 ppm) or the impurity metabolite PCBN (<0.008 ppm) were noted.

In studies from Kenya (Africa), crops had received two or 12 applications at respective rates of 1.4X and 1X proposed, and samples were collected at 29 days after the final application. The coffee beans were removed from the berries and analyzed. No detectable residues of chlorothalonil (<0.05 ppm), its metabolite (<0.05 ppm), or the impurities were noted.

Under the proposed use, coffee can be harvested on the day of treatment (0-day). There are no 0-day data which reflect the proposed use. (Data are available for 1X rate with a 3-day PHI and 0.34X and 0.75X at 0-day PHI.) The 0-day data at 0.75X and the 3-day data at 1X approximate residues expected from the proposed use.

The proposed tolerance level of 0.05 ppm is not adequate. A level of 0.2 ppm is adequate to cover residues likely to result from the proposed use. This level will be sufficient to cover expected variations in residue levels.

Coffee Processing

The coffee berry is picked from the branch, pulped at the mill (the outside covering is removed) which leaves two small beans. The beans are dried in the sun or by machine, further cleaned to remove membrane around bean and graded. This component is known as green coffee (the RAC) and is ready for roasting.

The coffee bean is roasted for 15-20 minutes at 450-500°F, and are then quenched with water which is driven off as steam.

The roasting process should considerably reduce any residues present on the green bean. Therefore, residues, if any, on the roasted bean would be less than the level on the rac.

For instant or powdered coffee, the roasted beans are ground, washed with water which extracts solubles, filtered and dried at greater 200°F. Residues in the roasted, if any, would have been reduced in the powdered coffee. Therefore, any residues present in powdered coffee would be considerably less than the level in the rac.

The brewed coffee resulting from the treated rac would contain a lower level of residues. This follows from the dilution effect in brewing coffee as well as the fact that the roasted bean would have a lower residue level than the rac.

In view of the foregoing, we conclude that residues in processed coffee (roasted coffee, powdered coffee) or brewed coffee, if any, would be considerably less than the level in the green coffee (RAC).

In support of the foregoing conclusion, the FDA has shown that 10 percent of the residue in the green bean survives the roasting process. (U.S. DHEW, FDA Compliance Program Evaluation, FY 77/78, "Pesticides in Imported Coffee Beans".)

Meat and Milk

No feed items are involved in this petition. Therefore, no residues will occur in eggs, milk, and meat of livestock as a result of the proposed uses.

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL CHLOROTHALONIL PETITION NO. 2E2744

CCPR NO. 81

Codex Status	Proposed U.S. Tolerances
/___/ No Codex Proposal Step 6 or above	2,4,5,6-tetrachloro-isophthalonitrile and its metabolite 4-hydroxy-2,5,6-trichloro-isophthalonitrile
Residue (if Step 9):	Residue:
Crop(s) Limit (mg/kg)	Crop(s) Tol. (ppm)
none (on these commodities)	cocoa beans 0.05 coffee beans 0.05
CANADIAN LIMIT	MEXICAN TOLERANCIA
Residue:	Residue:
Crop Limit (ppm)	Crop Tolerancia (ppm)
None (on these commodities)	None (on these commodities)

Notes: