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

MAR 19 1984

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#2G2660. Chlorothalonil on apples. Request for extension of temporary tolerance and 677-EUP-22. Accession #072097.

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and

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SDS Biotech Corporation, which has received the EPA registration for Bravo 500 from Diamond Shamrock Corporation, requests an EUP for the fungicide chlorothalonil(tetrachloroisophthalonitrile) on apples from March 1, 1984 through May 31, 1984. A temporary tolerance is proposed for chlorothalonil and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile at 0.1 ppm on apples. The labeling for a previous EUP on apples, 677-EUP-22, restricted application to apples for the fresh market only since no residue data were available for apple juice, wet apple pomace, and dried apple pomace. Additional residue data on processing fractions are now submitted. The use is also now expanded to include aerial as well as ground application.

A previous temporary tolerance for 2,4,5,6-tetrachloroisophthalonitrile and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile in or on apples at 0.1 ppm expired on 7/1/83.

Under the proposed EUP, a total of 1500 gallons Bravo 500 (6255 lbs. a.i.) will be shipped for use on a total of 700 acres in the states of IL, IN, KY, ME, MA, MI, MO, NY, NC, OH, PA, VA, WA and WI.

Conclusions

1. The nature of the residue is adequately defined. Chlorothalonil (DS-2787) and 4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) are the residues of concern.

2. Adequate analytcal methods are available for enforcement of the proposed temporary tolerance.

3a. Residues in apples resulting from ground application will not exceed the proposed temporary tolerance of 0.1 ppm. No residue data reflecting aerial application are submitted.

3b. Residues do not concentrate in juice.

3c. Residues concentrate in wet and dry apple pomace by factors of 3 in wet apple pomace and 10 in dry apple pomace. Temporary tolerances should be proposed for wet apple pomace at 0.3 ppm and for dry apple pomace at 1.0 ppm.

3d. No residues of hexachlorobenzene or pentachlorobenzonitrile were found on apples as a result of use of Bravo 500.

4a. As there are no poultry feed items involved with this use, there will be no problem with secondary residues in poultry and eggs. This use falls in Category 3 of Section 180.6(a) for poultry and eggs.

4b. Trace residues may result in meat and milk from feeding dry apple pomace with chlorothalonil residues of 1.0 ppm to cattle in 50% of the diet. The residues are not expected to exceed the method sensitivities of 0.03 ppm in milk and 0.1 ppm in the meat, fat and meat by-products of cattle. Temporary tolerances of 0.03 ppm in milk and 0.1 ppm in meat should be proposed.

Recommendation

We recommend that the proposed temporary tolerance not be established because of the reasons cited in conclusions 3a, 3c and and 4b.

We could recommend for the proposed temporary tolerance if temporary tolerances were proposed for wet apple pomace at 0.3 ppm, dry apple pomace at 1.0 ppm, milk at 0.03 ppm, and the meat fat and meat by-products of cattle at 0.1 ppm, and provided Section B were revised to limit applications to ground application.

Detailed Considerations

Manufacture

We refer to the RCB review of PP#4E1502 (R. Schmitt, 11/27/74) for a discussion of the manufacturing process for technical chlorothalonil.

In the RCB review of PP#8E2065 (McLaughlin, 11/30/78), it was determined that impurities in technical chlorothalonil are hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN). Of 308 batches which were analyzed, [redacted]

PRODUCT IMPURITY INFO IS NOT INCLUDED

Formulation

The formulation to be used is Bravo 500. Bravo 500 is a dispersible suspension which contains 4.17 lb. active ingredient per gallon. All inerts in Bravo 500 are cleared under 40 CFR 180.1001.

Proposed Use

Under the EUP, one application will be made on apple trees at the rate of 2-4 gals. Bravo 500/A (8.34-16.68 lb. a.i./A) at the 1/4 inch green stage of bud expansion to protect against the primary infection stage of scab. The fungicide will be applied in 300-400 gals. water/A for ground application of dilute sprays or in 15-100 gals. water/A for concentrate ground sprays or aerial applications. Bravo 500 may be applied after an oil application provided an interval of at least 48 hours is observed between applications. Do not allow livestock to graze treated areas.

Nature of the Residue

The metabolism of chlorothalonil was discussed in N. Dodd's review of 7/19/82. We concluded then that chlorothalonil and 4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) are the residues of concern. We also consider the impurities in technical chlorothalonil, hexachlorobenzene and pentachlorobenzonitrile, to be of concern if present.

Analytical Method

Document #607-3CR-83-0005-001:

Chlorothalonil and DS-3701 are extracted from apples and processed products with acetone acidified with sulfuric acid. After fil-

tration, acetone is evaporated and the residue redissolved in 0.4M sodium bicarbonate. The pH is adjusted to 4.5 using 0.4M sodium bicarbonate or dilute sufluric acid. Residues of chlorothalonil are selectively partitioned from the aqueous phase (which (which contains DS-3701) into a petroleum ether phase. After addition of 0.4 ml of 2% paraffin oil in petroleum ether, the ether evaporated. The aqueous phase containing DS-3701 is acidified with sulfuric acid to a pH of less than 2. The residue is extracted from the aqueous phase with a solution of petroleum ether and diethyl ether. After evaporation of the ether, the DS-3701 is converted to the methyl ether by reacting the dried residue with 5 ml methylating agent and 10 ul 1:3 concentrated hydrochloric acid: methanol and then with 3 additional ml methylating agent. (The methylating agent is 3-methyl-1-p-tolyl-triazene (MTT) in diethyl ether.) If necessary, the residues of chlorothalonil and methylated DS-3701 are cleaned up by column chromotography. The residues are quantitated by electron capture gas chromatography. Recoveries of chlorothalonil on apples and apple products were 64-140% at fortification levels of 0.05 to >1 ppm. Recoveries of DS-3701 on apples and apple products were 60-120% at fortification levels of 0.05 to >1 ppm. (Apple products include apple cores and peels, apple slices, apple sauce, apple juice, wet apple pomace, dry apple pomace, hammermill apples, and apple cider.) The sensitivity of the method for apple products is 0.01 ppm DS-2787 and DS-3701. The method sensitivity for water is 0.001 ppm DS-2787 and DS-3701.

Document #619-3CR-0009-001:

The analytical method used to analyze chlorothalonil, DS-3701 HCB, and PCBN on apples is similar to the method used in Document #607-3CR-83-0005-001. Chlorothalonil, DS-3701, HCB, and PCBN are extracted from apples with acetone acidified with sulfuric acid. After filtration, acetone is evaporated and the residue redissolved in 0.4 M sodium bicarbonate. The pH is adjusted to 4.5 using 0.4 M sodium bicarbonate or dilute sulfuric acid. Residues of chlorothalonil, HCB, and PCBN are selectively partitioned from the aqueous phase (which contains DS-3701) into a petroleum ether phase. After addition of 0.2 ml of 2% paraffin oil in petroleum ether, the ether is evaporated. The residues are redissolved in a solution of 20% methylene chloride and 80% hexane. The residues of chlorothalonil, HCB, and PCBN are cleaned up and separated by column chromatography. The aqueous phase containing DS-3701 residues is processed as discussed above in connection with Document #607-3CR-83-0005-001. Residues of chlorothalonil, HCB PCBN and DS-3701 are determined by electron capture gas chromatography. Recoveries were determined by spiking apples at concentrations of 0.1-10.0 ppm for chlorothalonil, 0.05-0.5 ppm for DS-3701 ,0.01-0.05 ppm for HCB, and 0.02-0.10 ppm for PCBN. Recoveries were 60-101% for chlorothalonil, 64-80% for DS-3701, 80-97% for HCB, and 85-108% for PCBN. The sensitivity of the method is 0.03 ppm DS-2787, 0.03 ppm DS-3701, 0.004 ppm HCB and 0.008 ppm PCBN.

The analytical method used in Document #607-3CR-83-0005-001 is one or 3 discussed in the review of PP#2G2660 dated 7/19/82. The enforcement method contained in PAM II for determination of chlorothalonil and its 4-hydroxy-metabolite (DS3701) involves extraction of the parent and metabolite with acidified acetone, separation of the two compounds on a Florisil column, methylation of the metabolite, and determination of the derivative and parent by MC or EC-GLC. This method is validated in PAM II for potatoes.

We conclude that adequate analytical methods are available for enforcement of the proposed temporary tolerance.

Residue Data

Residue data submitted with this petition are on residues in the raw agricultural commodity (Document #619-3CR-83-0009-001) and in processing fractions (Document # 607-3CR-83-0005-001).

Document #619-3CR-83-0009-001:

Eleven studies on apples were conducted in eight states of CA, MI, NY, OH, OR, VA, WA and WI to determine residues of chlorothalonil, 4-hydroxy-trichloroisophthalonitrile (DS-3701), hexachlorobenzene, and pentachlorobenzonitrile on apples. The Bravo 500 formulation which was used contained 40.6% chlorothalonil, 0.33% PCBN, and 0.02% HCB. A single early season application of Bravo 500 at the 1/4 inch green tip stage of bud development was made. Application rates were 1-10 gals Bravo 500/A (4.17-41.7 lbs. a.i./A), up to 2.5X. Preharvest intervals ranged from 132-196 days. No detectable residues of DS-3701, HCB, or PCBN were found in the 11 studies. No detectable residues of chlorothalonil were found in 6 of the 11 studies. Detectable residues of chlorothalonil reflecting 1 or 2 applications at the rate of 2 gals of Bravo 500/A (8.34 lb. a.i./A), 0.5X the recommended rate, were a maximum of 0.04 ppm. The remaining detectable residues (0.04-0.09 ppm) reflected application rates of 8 or 10 gals. Bravo 500/A (33.36 or 41.7 lbs. a.i./A), up to 2.5X the recommended maximum application rate.

Document #607-3CR-83-0005-001:

Apples from Michigan were processed into frozen apple slics, applesauce, apple juice, apple peels/cores, and dried apple pomace. One lot of apples was sprayed once using ground equipment with 4 gals. Bravo 500/acre (16.68 lbs a.i./A) at the 1/4 inch green stage of bud expansion. One lot was treated with 6.5 gals. Bravo 500 /A (27.1 lb. a.i./A) 7 days before harvest in order to obtain weathered residues for the processing study.

Residues in apples and processing fractions resulting from the treatment at 16.68 lbs a.i./A were as follows: a maximum of 0.02 ppm chlorothalonil and no detectable (<0.01 ppm) DS-3701 in unwashed whole apples, no detectable chlorothalonil or DS-3701 on washed whole apples, 0.001 ppm chlorothalonil and no detectable DS-3701 (<0.001 ppm) in wash water from the commercial processing of apples, 0.01-0.06 ppm chlorothalonil and no detectable DS-3701 on apple peels and cores, no detectable chlorothalonil or DS-3701 in apple slices, unsweetened or sweetened applesauce, canned apple juice or apple cider;0.01-0.09 ppm chlorothalonil and no detectable DS3701 in wet apple pomace, 0.05-0.38 ppm chlorothalonil and no detectable DS-3701 in dry apple pomace, and 0.02-0.03 ppm chlorothalonil and no detectable DS-3701 in hammermill apples.

Residues in apples and processing fractions resulting from the spike treatment at 27.1 lb. a.i./A were as follows: 3.69-5.24 ppm chlorothalonil and no detectable DS-3701 on unwashed whole apples, 3.39-4.30 ppm chlorothalonil and no detectable DS-3701 on washed whole apples, 2.10-2.53 ppm chlorothalonil and 0.005-0.006 ppm DS-3701 in wash water, 15.30-19.47 ppm chlorothalonil and no detectable DS-3701 in apple peels and cores, 0.12-0.21 ppm chlorothalonil and no detectable DS-3701 in apple slices, 0.01-0.02 ppm chlorothalonil and a maximum of 0.04 ppm DS-3701 in unsweetened applesauce, 0.02 ppm chlorothalonil and no detectable DS-3701 in sweetened applesauce, 9.54-15.34 ppm chlorothalonil and a maximum of 0.01 ppm DS3701 in wet apple pomace , 37.00-49.28 ppm chloro thalonil and 0.06-0.09 ppm DS-3701 in dry apple pomace, 0.09-0.10 ppm chlorothalonil and no detectable DS-3701 in canned juice, 4.06-4.40 ppm chlorothalonil and no detectable Ds-3701 in hammermill apples, and 2.86-3.04 ppm chlorothalonil and no detectable DS-3701 in apple cider.

Residues in Processed Fractions Resulting from Early Season Application of 4 gals. Bravo 500/A

	Chlorothalonil(ppm)	DS-3701(ppm)
Whole Apples (unwashed)	$\leq$ 0.02	ND
Whole Apples (washed)	ND	ND
Peels & Cores	0.01-0.06	ND
Apple Slices	ND	ND
Applesauce	ND	ND
Apple Juice	ND	ND
Wet Apple Pomace	0.01-0.09	ND
Dry Apple Pomace	0.05-0.38	ND
Hammermill apples	0.02-0.03	ND

ND - <0.03 ppm.

Residues in Processed Fractions Resulting from Spike Treatment to Obtain Weathered Residues

	Chlorothalonil(ppm)	DS-3701(ppm)
Whole Apples(unwashed)	3.69 - 5.24	ND
Whole Apples (washed)	3.39 - 4.30	ND
Peels & Cores	15.30 -19.47	ND
Apple Slices	0.12 - 0.21	ND
Applesauce (unsweetened)	0.01 - 0.02	$\leq$0.04
Applesauce (sweetened)	0.02	ND
Wet Apple Pomace	9.54 -15.34	$\leq$0.01
Dry Apple Pomace	37.00 -49.28	0.06-0.09
Canned Apple Juice	0.09 - 0.10	ND
Hammermill Apples	4.06 - 4.40	ND
Apple Cider	2.86 - 3.04	ND

Concentration of Residues in Processing Fractions

Whole Apples (unwashed)	Wet Apple Pomace	Concentration Factor
3.69-5.24 ppm	9.54-15.34 ppm	3

Whole Apples (unwashed)	Dry Apple Pomace	Concentration Factor
3.69-5.24 ppm	37.00-49.28 ppm	10

We conclude that residues in whole apples resulting from ground application will not exceed the proposed temporary tolerance of 0.1 ppm on apples. No residue data reflecting aerial application are submitted. Residues do not concentrate in juice. Residues do concentrate in wet and dry apples pomace by factors of 3 in wet apple pomace and 10 in dry apple pomace. Temporary tolerances should be proposed for wet apple pomace at 0.3 ppm and for dry apple pomace at 1.0 ppm. No residues of hexachlorobenzene or pentachlorobenzonitrile were found on apples as a result of use of Bravo 500.

Meat, Milk, Poultry and Eggs

No new data for meat, milk, poultry, and eggs are submitted with this petition. Residue data on meat and milk which were submitted in connection with PP#1F1024 are discussed in a previous review to which we refer (PP#2G2660, N. Dodd, 7/19/82).

We conclude that there will be no problem with secondary residues in poultry and eggs since cull apples are not a significant feed item and since we do not consider dried apple pomace to be a poultry feed item. The use falls in Category 3 of Section 180.6(a) for poultry and eggs.

We conclude that trace residues may result in meat and milk from feeding dry apple pomace with chlorothalonil residues of 1.0 ppm to cattle in 50% of the diet. The residues are not expected to exceed the method sensitivities of 0.03 ppm in milk and 0.1 ppm in meat. Temporary tolerances of 0.03 ppm in milk and 0.1 ppm in meat, fat, and meat byproducts of cattle should be proposed. This use falls in Category 2 of Section 180.6(a) for meat and milk.

cc: RF, Circu, N. Dodd, SF, PP#2G2660, TOX, EEB, EFB, FDA, Robert Thompson
RDI:E.Zager:EZ:3/15/84:R.D.Schmitt:RDS:3/15/84
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