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

APR 27 1987

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: EPA Registration No. 279-3014. PP #1F2476. Permethrin on field corn. Amended registration for full season use on corn. (RCB #1520) Accession No. 265258

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THRU: Charles L. Trichilo, Chief
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TO: George LaRocca, Product Manager No. 15
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and

Toxicology Branch
Hazard Evaluation Division (TS-769)

FMC Corporation is requesting amended registration of permethrin (Pounce 3.2 EC, Reg. No. 279-3014) to allow the use on field corn throughout the full corn season.

Pounce 3.2 EC is an emulsifiable concentrate formulation containing 3.2 lbs. a.i./gal.

A permanent tolerance has been established for residues of permethrin per se [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl) 2,2-dimethylcyclopropane carboxylate] on cottonseed at 0.5 ppm under 40 CFR 180.378 (a).

Under 40 CFR 180.378 (b), tolerances have been established for residues of permethrin and the sum of its metabolites 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid (DCVA) and (3-phenoxyphenyl)methanol (3-PBA) on a number of raw agricultural commodities including corn fodder and forage at 60 ppm, sweet corn (K + CWHR) at 0.1 ppm, and corn grain (field and pop) at 0.05 ppm.

Under 40 CFR 180.378 (c), tolerances have been established on animal commodities for residues of permethrin and the sum total of its metabolites DCVA, 3-PBA and 3-phenoxybenzoic acid. These tolerances range from 0.05 ppm in eggs, poultry fat, poultry meat, and poultry meat by-products to 2.0 ppm in the fat of cattle, goats, hogs, horses, and sheep and 3.75 ppm in milk fat, reflecting 0.15 ppm in whole milk.

Exclusive use notification waiver letters for Pounce 3.2 EC were submitted from Wellcome Research Laboratories, Fairfield American Corporation, Zoecon Industries, ICI Americas, Inc., and W.C. Miller Co. ICI had also submitted a petition for residues of permethrin on field corn in PP #2F2624 and on sweet corn in PP #9F2207 and PP #3F2781. The letter from ICI (from R.E. Ridsdale, ICI to G. LaRocca, EPA, RD) authorizes the use of any data contained or referenced in ICI Americas Inc. files for EPA Reg. No. 10182-17 and 10182-18 in support of FMC's registration for products containing permethrin for a number of crops, including the full season use on field corn.

Registered Use

Permethrin had been registered for use on field corn for preemergent use and for foliar application. Preemergent use is permitted from five days before planting to emergence of the crop. The application rate is 0.2 lb. a.i./A as a broadcast spray with ground equipment.

The post ermergent use was originally limited to application prior to ear formation at rates of 0.2 lb. a.i./A using ground or aerial equipment or by injection into overhead sprinkler irrigation water. The use was subsequently amended to permit use prior to the brown silk stage (see memo of S. Malak, 7/22/85, EPA Registration No. 279-3014).

Proposed Use

The preemergent application rate and timing of application remain the same. Application may be made as a broadcast spray as before or as a banded application. Aerial application is also permitted. Tank-mixtures with a number of herbicides (tabulated below) are also permitted.

AAtrex	Lasso	Prowl
Banvel	Lorox	Ramrod
Bladex	Paraquat	Roundup
Dual	Princep	Sutan
Eradicane		

The applicator is warned to observe all restrictions and precautions appearing on the labels of these products, which are all registered for use on field corn.

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Foliar applications at a rate of up to 0.2 lb. a.i./A by ground equipment (10 gallons of finished spray per acre) or air equipment (1 gallon finished spray per acre) are permitted. Pounce may also be injected into overhead sprinkler irrigation water provided that an anti-backflow check valve is present and a check valve is present to prevent irrigation water from entering the chemical supply tank. The irrigation injection system must also have interlocking on-off switches. No more than 0.6 lb. a.i./A may be applied per season.

RCB has no objection to the use of banded applications or aerial equipment during the preemergent period.

No PHI is stipulated. In the original submission of PP #1F2476, the petitioner had specified a 30 day PHI. The petitioner needs to submit a revised Section B/label in which he specifies the intended PHI, which should be adequately reflected by the residue data.

Nature of the Residue

Plants

The metabolism of permethrin by snapbeans, cotton, soybeans, potatoes, and cabbage have been previously reported (PP #7G1891, 3/10/77, memo of A. Rathman; PP #8G2029, 12/27/78, memo of A. Rathman; PP #0F2389, 4/10/81, memo of J.H. Onley). The residues of concern are permethrin and the acid [3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid or DCVA] and alcohol [(3-phenoxyphenyl)methanol or 3-PBA] resulting from cleavage of the parent ester.

Animals

Metabolism studies of permethrin by chickens, cows, goats, and rats have been submitted and reviewed in conjunction with PP #8F2034 and PP #8F2044. In addition to the plant metabolites DCVA and 3-PBA, 3-phenoxybenzoic acid has been identified as an animal metabolite and is included in the tolerance expression under 40 CFR 180.378 (c).

Analytical Methodology

Permethrin

The procedure for the analysis of whole unsteeped grain, gluten feed, gluten meal, starch, and extracted germ meal was essentially the same as that described in PAM II. These samples were extracted with hexane/2-propanol, washed with water, and the organic extract was dried by passage through anhydrous sodium sulfate. The extracted germ meal was further cleaned up by gel permeation chromatography (GPC) and chromatography on Florisil before quantitation with GLC using a ^{63}Ni electron capture detector and a column packed with 1% SP2330. Soapstock was diluted with water

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(pH 6.2), the aqueous sample was extracted with methylene chloride, and the organic layers were concentrated and cleaned up by GPC. After Florisil clean-up, the soapstock residues were analyzed by GLC as described above. The oils (crude, refined, bleached or deodorized) were diluted in either cyclohexane/methylene chloride or ethyl acetate/hexane and subjected to GPC, Florisil clean-up, and GLC. Concentrated steepwater was blended with methanol, and filtered. The filter cake was blended with methanol/water (2:1), the extract was extracted with hexane, and the hexane extracts were cleaned up by chromatography on Florisil before quantitation by GLC. The whole unsteeped grain, the gluten feed, gluten meal, starch, and steepwater omitted the GPC clean-up, which was used in working up the extracted germ meal, oils, and soapstock.

DCVA

The procedure for the analysis of DCVA is similar to that described in PAM II. Samples of whole unsteeped grain, gluten feed, gluten meal, starch, extracted germ meal and concentrated steepwater were blended with methanol or methanol-water. Oils were dissolved in methylene chloride. The pH of all the extracts was adjusted to 8.3 and extracted with methylene chloride, or, in the case of steepwater, with hexane. The organic layers were back-extracted with 0.01 N sodium hydroxide. The methylene chloride containing the oil was simply extracted twice with water (pH 8.3), and the organic layer was then discarded. The alkaline aqueous fractions were concentrated, acidified, and refluxed. The DCVA was extracted from the hydrolysate by passing the sample through a C18 cartridge. DCVA was eluted from the cartridge with methylene chloride, concentrated, and derivatized with pentafluorobenzyl bromide (PFB) using tetrabutylammonium phosphate as a phase transfer agent. After clean-up by Florisil chromatography, the DCVA derivatives were determined by GLC on a 30 M DB-1 fused silica capillary column. A splitless mode of injection and a mass selection detector (MSD) were used.

The petitioner was unable to devise a method for the analysis of DCVA in soapstock. DCVA could not be separated from the fatty acids in soapstock.

The derivatives are known to be somewhat unstable; therefore known amounts of DCVA were carried through the derivatization and Florisil clean-up steps and used for quantitation.

3-PBA

The petitioner chose to analyze free and conjugated 3-PBA separately, although in the PAM procedure the residues freed by hydrolysis are combined with any free 3-PBA before derivatization.

Samples of whole unsteeped grain, gluten feed, gluten meal, starch, extracted germ meal, and steepwater were blended with methanol (steepwater) or methanol/water. The extracts were concentrated on a rotatory evaporator, diluted with water, and

extracted witih methylene chloride. Oils were disssolved in methylene chloride and extracted with water (pH 8.3).

The methylene chloride phases could contain free 3-PBA, while the aqueous phase could contain conjugates of 3-PBA. The methylene chloride extracts were concentrated and the residues were dissolved in toluene for derivatization with HFBA, although an additional GPC step was needed before derivatization in the case of the oils. The aqueous extracts were acidified and hydrolyzed to release 3-PBA. 3-PBA was removed from the hydrolysate by passing the sample through a C18 cartridge and was eluted from the cartridge with methylene chloride. Derivatization of the free 3-PBA from the methylene chloride extracts and from the hydrolysis was carried out with HFBA and pyridine. The HFBA derivatives were cleaned up by chromatography on Florisil for quantitation with GLC using an MSD and a DB-1 fused silica capilllary column.

Since the HFBA derivatives were known to be somewhat unstable, known amounts of 3-PBA were derivatized and carried through the Florisil clean-up for quantitation purposes.

The petitioner was not successful in devising a procedure which could determine residues of 3-PBA in soapstock.

Recoveries of permethrin, DCVA, and 3-PBA from wet corn milling fractions are given below. Recoveries of free 3-PBA resulted from spiking the matrix before extraction. Recoveries of "conjugated" 3-PBA reflect a second spike just before acid hydrolysis, after separation of the 3-PBA containing methylene chloride layer.

Matrix	Spike level (ppm)	% Recovery					
		Permethrin		DCVA		3-PBA	
		cis	trans	cis	trans	free	conjugated
Grain	0.05	86	94	96-104	90-140	80-88	100
	0.10	69	72				
Gluten feed	0.05	84	102	70-74	66-78	78-88	
	0.10	88	99				
Gluten meal	0.05	100	64	68-70	62-64	54-72	78-82
Starch	0.05	80	82	84-98	78-94	50-70	96
Extracted germ	0.05	52-56	66-74	88-90	78-84	60-64	64-72
Crude oil	0.05	84-104	74-96	60-68	50-56	76-112	82-104
	0.10	79	66	93-105	84-96	84	81

Matrix	Spike level (ppm)	% Recovery					
		Permethrin		DCVA		3-PBA	
		cis	trans	cis	trans	free	conjugated
Refined oil	0.05	64-82	62-66	72-80	80-96	106	84
	0.10	73	57			128	93
	0.50-1.0					93-97	78-88
Bleached oil	0.05	68	76			90	
	0.10	87	68	101	97	110	
Deodorized oil	0.05	74	74			78	96
	0.10	88	70	102	99	83	118
Soapstock	0.05	72-82	68-74	---	---	---	---
Steep-water	0.05	58-60	66	74-76	86	50-54	52-58

A method sensitivity of 0.05 ppm (for each isomer) is claimed for permethrin analyses in all matrices. A method sensitivity of 0.05 ppm (for each isomer) is claimed for DCVA analyses for all matrices except for oils, where the sensitivity ranges from 0.05-0.10 ppm, and soapstock. A method sensitivity of 0.05 ppm (for each isomer) is claimed for 3-PBA analyses in all matrices, except soapstock. Therefore the limit of determination for permethrin plus its metabolites would be about 0.25 ppm for any fraction. The method detectability was claimed to be about 0.01 ppm for each compound in all matrices except soapstock.

The petitioner has submitted representative chromatograms of check, fortified, and treated samples of starch, crude oil, and steepwater reflecting permethrin analyses, chromatograms of check, fortified, and treated samples of extracted germ meal, refined oil, and steepwater reflecting DCVA analyses, and chromatograms of check, fortified, and treated samples of deodorized oil, gluten feed, and steepwater reflecting analyses for 3-PBA.

RCB concludes that adequate analytical methodology was used to determine residues of permethrin in all matrices; adequate methodology was used to determine residues of DCVA and 3-PBA in all matrices except soapstock, for which no methodology is available. The petitioner will need to provide methodology for the determination of DCVA and 3-PBA in soapstock (see also RCB's Comments/Conclusions re: Processing Studies that follows in this review).

Residue Data

No new field residue data were submitted with the present amendment. Instead, the petitioner cites previously submitted data (PP #1F2476) reflecting 3 applications at a rate of 0.2 lb. a.i./A

(proposed rate, 3 x 0.2 lb. a.i./A) and PHI's ranging from 13-80 days (the proposed PHI is unspecified). The data had been reviewed earlier in the J.H. Onley memo of 5/26/81 and supported the use of permethrin on field corn prior to ear formation. Although the residue data also supported the proposed tolerance of 0.05 ppm, application prior to ear formation had been deemed necessary to achieve a no residue situation so that food/feed additive tolerances would not be necessary for corn oil and soapstock (PP #1F2476, memo of J.H Onley, 3/31/83). A corn fractionation study submitted by ICI Americas (PP #2F2624/2H5335) had indicated that residues of permethrin concentrate (10 X) in refined deodorized corn oil and soapstock; however, the Delaney Amendment of the Food Drug and Cosmetic Act (FD & C) forbids the establishment of tolerances of carcinogens on processed foods and feeds.

FMC now proposes a full season use of permethrin on corn. No PHI is stipulated in the submitted Section B/label. The registered use of permethrin on corn permits application prior to brown silk formation. This stage ordinarily occurs 45-50 days before harvest (see memo of S. Malak, EPA Registration No. 279-3014, 7/22/85). RCB has previously concluded that a tolerance of 60 ppm would adequately cover residues expected to arise on fodder and forage treated 0-1 day before harvest (see PP 3F2781, permethrin on sweet corn, memo of J.H. Onley, 2/17/83).

The corn grain residue data which are available for PHI's of less than 45 days are tabulated below. No detectable residues of DCVA or 3-PBA were reported on any grain samples. The table includes information submitted by ICI Americas in support of PP #2F2624.

Site	Application rate	PHI (days)	Permethrin residues (ppm)
CO**	2 x 0.1	0	ND**
GA**	5 x 0.2	1	ND**
TX**	5 x 0.2	1	0.003
TX**	2 x 0.1	1	0.01
TX**	5 x 0.2	4	0.031
NM**	3 x 0.1	11	trace
KS*	3 x 0.2	13	0.02
NB**	5 x 0.2	14	0.031
KS*	3 x 0.2	15	0.01
NB**	5 x 0.2	16	<0.006
KS*	3 x 0.2	21	0.02
OK*	3 x 0.2	21	0.01
KS*	3 x 0.2	22	ND*
KS*	3 x 0.2	22	ND*
KS*	3 x 0.2	28	ND*
CO**	3 x 0.2	28	ND**
SD**	5 x 0.2	28	0.033
SD**	5 x 0.2	28	ND (<0.01)
TX*	3 x 0.2	36	ND*
KS*	3 x 0.2	36	ND*

Site	Application rate	PHI (days)	Permethrin residues (ppm)
CO**	3 x 0.2	41	ND**
AR*	3 x 0.2	41	ND*
LA*	3 x 0.2	41	ND*
KS*	3 x 0.2	44	0.01

* Data supplied by FMC; ND=<0.01 ppm per isomer; PP #1F2476
** Data supplied by ICI; ND=<0.05 ppm total permethrin; PP #2F2624

From the residue data, it appears that real residues of permethrin occur at the shorter PHI's. Out of the 45 trials, detectable residues were reported in 12 trials; 10 of these trials involved PHI's of less than 45 days. A permethrin residue level of 0.01 ppm was reported from one OH trial, which observed a PHI of 58 days (3 x 0.2 lb. a.i./A; submitted by FMC). A permethrin residue level of 0.013 ppm was reported from a trial in NB, which observed a PHI of 54 days (3 x 0.2 lb. a.i./A; submitted by ICI).

Of the 24 field trials with PHI's of less than 45 days, 14 trials, located in OK, KS, CO, GA, NB, TX, and NM, reflect PHI's of 3 weeks or less, 5 trials, located in KS, CO, GA, NB, TX, and NM, reflect PHI's of 2 weeks or less, and 5 trials, located in CO, GA, and TX, reflect PHI's of less than 4 days.

In order to support a national tolerance on field corn, residue data reflecting the proposed use are needed from all areas of the country. Even though some of the data reflect exaggerated application rates (5 x 0.2 lb. a.i./A), RCB considers the available data to be far too skimpy to support PHI's of less than 45 days. Residue data from 3 trials using the higher rate exhibited residue levels of >0.03 ppm, which approaches the tolerance level (0.05 ppm). In order to support the proposed use on corn, residue data reflecting any intended PHI (whatever it may be) would be required from all field corn growing areas, especially the corn belt. The shortest PHI observed in corn belt field trials was 46 days (IA).

Corn Fractionation Study

Dry Milling Process

Residue data on processed corn fractions had been submitted by ICI in support of PP #2F2624. The distribution of residues among the various dry milling fractions is given below.

	Control (ppm)				Treated (ppm)			
Sample	Per	DCVA	3-PBA	Sum	Per	DCVA	3-PBA	Sum
Whole corn	Tr	ND	ND	Tr	0.031[a]	ND	ND	0.031
Meal	Tr	ND	ND	Tr	0.109[b]	ND	ND	0.109
Crude oil	0.12	ND	0.027[c]	0.15	0.19	0.017	0.037	0.24

Sample	Control (ppm) Per	DCVA	3-PBA	Sum	Treated (ppm) Per	DCVA	3-PBA	Sum
Refined, bleached deodorized oil	0.09	0.003	0.037	0.13	0.14	0.004	0.027	0.17
Soapstock	0.07	0.02	0.027	0.12	0.11	0.013	0.058[d]	0.18

[a] Taken from lab sheet; reported as 0.16 on one summary, as 0.031 on a second summary
[b] Higher value from lab sheets; reported as 0.037 on one summary, as Tr on a second summary
[c] Higher value from lab sheets; reported as 0.040 and 0.037 on summaries
[d] Higher value from lab sheets; reported as 0.080 on summaries

Wet Milling Process

The petitioner has submitted a letter from T. Gardner, RD, to Dr. M.W. Galley, FMC, in which the Agency agrees that a protocol which calls for spiking corn with cypermethrin before processing would be appropriate. The petitioner has extended this approval to permethrin, a similar compound.

Corn ears were sprayed with a dilute solution of permethrin, DCVA, and 3-PBA in acetone and allowed to dry. The corn grains were removed from the ears and analyzed. The treated grain was subjected to a simulated wet milling process to yield gluten feed, gluten meal, starch, germ, and partially concentrated steep-water. The germ was processed to yield crude oil and extracted germ meal.

Light steepwater was obtained from the A.K. Staley Manufacturing Company. The corn (4 kg) was added to a steeping vessel with 7.5 liters of active steepwater. A peristaltic pump was used to recirculate the steepwater from the bottom of the vessel to the top, and the vessel was rotated at a speed of 60 rpm to simulate the turbulence that occurs during industrial steeping as the steepwater is moved from tank to tank. The corn was steeped for 36 hours. The temperature was continuously monitored; the temperature rose from about 30°C to 45-47°C after about 4 hours and was maintained there until 24 hours, when the temperature was increased to 52-54°C. The pH was maintained at pH 4.0-4.2. Every 4 hours, the steepwater was analyzed for pH, SO_2, viable cell count, lactic acid, soluble carbohydrates, and total dry solids. At 36 hours, the content of the steeping vessel was vigorously mixed, and the steepwater was drawn off and concentrated to about 1/2 its original volume under a partial vacuum at 65°C. The steeped corn was manually separated into endosperm, germ, and hull. The endosperm was blended with water and crushed ice for 12-15 minutes in a kitchen

blender, and the resulting slurry was centrifuged for 30 minutes at 45,000 rpm. The supernatant was discarded; the remaining solid consisted of two layers: a yellow top layer, which was mainly gluten, and an off-white bottom layer of starch. Samples of the starch, the starch/gluten interface, and the remaining starch were removed, dried, and stored until analysis.

The corn germ sample (moisture content, ≈10%) was ground in a Waring Blender, sieved, heated for one hour at 120°C in a pressure vessel with water placed external to the sample container, placed in a "Butt" tube, and extracted with refluxing hexane. After 3.5 hours, the sample was reground and reextracted for an additional 2.5 hours. The crude oil was heated to 65°C and treated with sufficient 14° Be' NaOH to neutralize an assumed 5% free fatty acid content plus 1.4% excess. A temperature of 65-70°C was maintained for 5 minutes, and the layers were allowed to separate to yield refined oil and an aqueous layer containing soapstock.

Processing of Spiked Oil

A sample of crude oil was spiked with permethrin, DCVA, and 3-PBA and carried through a refining process that included refining, bleaching, and deodorizing. According to the petitioner, details of both oil processing trials, conducted by Richard H. Purdy, Inc., are contained in Appendix B.

The residue levels of the various corn fractions are given in the table below. With the exception of check samples of crude and refined oil, all check samples were reported as non-detectable (<0.01 ppm) for all analytes. A check sample of crude oil was reported as containing 0.02 and 0.03 ppm respectively of cis and trans DCVA. A check sample of refined oil was reported as containing 0.01 ppm cis DCVA.

Fraction	Residue (ppm)					
	Permethrin		DCVA		3-PBA	
	cis	trans	cis	trans	Free	Conj
Unsteeped grain	0.11	0.11	(0.03)[a]	(0.04)	0.11	ND
Gluten feed	(0.04)	(0.04)	(0.02)	(0.02)	0.07	ND
Gluten meal	ND	ND	(0.04)	(0.04)	0.09	ND
Starch	ND	ND	ND	ND	(0.03)	ND
Extracted germ meal	ND	ND	(0.01)	(0.02)	(0.02)	ND
Crude oil	(0.02)	ND	0.29	0.39	0.92	(0.01)

Fraction	Residue (ppm)					
	Permethrin		DCVA		3-PBA	
	cis	trans	cis	trans	Free	Conj
Refined oil	ND	ND	ND	ND	0.66	ND
Soapstock	ND	ND	---[b]	---[b]	---[b]	---[b]
Steepwater	0.16	0.14	ND	ND	ND	ND
Spiked crude oil	0.12	0.11	0.50	0.41	0.55	ND
Refined oil	0.07	0.05	---[c]	---[c]	0. 4	ND
Bleached oil	0.08	0.05	(0.01)	ND	0.58	---[c]
Deodorized oil	(0.01)	ND	ND	ND	ND	ND

ND = non-detectable (<0.01 ppm per isomer)
[a] numbers in parentheses are estimates and are below the limit of determination, 0.05 ppm
[b] not analyzed; no methodology available
[c] not analyzed

The concentration factors of each residue in the various fractions as well as for the summed residues are given below.

Fraction	Concentration Factors		
	Permethrin	DCVA	3-PBA
Unsteeped grain	---	---	---
Gluten feed	<1X	<1X	<1X
Gluten meal	<1X	1.1X	<1X
Starch	<1X	<1X	<1X
Extracted germ meal	<1X	<1X	<1X
Crude oil	<1X	9.5X	9.2X
Refined oil	<1X	<1X	6.5X

Fraction	Concentration Factors		
	Permethrin	DCVA	3-PBA
Soapstock	<1X	---	---
Steepwater	1.5X	<1X	<1X
Spiked crude oil	---	---	---
Refined oil	<1X	---	1.1X
Bleached oil	<1X	<1X	1X
Deodorized oil	<1X	<1X	<1X

The petitioner has reported that residues of permethrin concentrate in partially concentrated steepwater, which is a feed ingredient. The petitioner argues that a feed additive tolerance is not needed on steepwater because it is not an end use product; it is always blended with other ingredients.

RCB's Comments/Conclusions, re: Processing Studies

The data from the dry milling processing study (submitted by ICI) indicated that permethrin and its metabolites concentrated in meal, refined, bleached and deodorized oil, and in soapstock. But the food/feed additive tolerances which are needed to cover the residues resulting from this concentration may not be established because of the Delaney amendment. It had therefore been necessary to amend the proposed use so that no detectable residues would be expected on corn grain, and application was limited to the period preceding ear formation.

The petitioner is now proposing a full season use on field corn, an application which, according to the available residue data, will result in detectable levels of permethrin/metabolites on corn grain. Processing of corn by both dry milling and wet milling is required whenever detectable residues are expected on the raw agricultural commodity. The petitioner cites statistics which indicate that wet milling accounts for about 70% of the corn which is used for food, alcohol, seed, or industrial products as opposed to 17% of this corn which is dry milled. Therefore, the petitioner argues, "...it becomes evident that the wet milling process is the appropriate way to run a corn processing study, and that the oil that is used as a food item is refined-bleached-deodorized oil."

Although more corn undergoes wet milling than dry milling, a tremendous amount of corn is dry milled because of the size of the nation's field corn crop. According to the petitioner's

submission, 150 million bushels of corn were dry milled in 1983. Therefore, an adequate dry milling study is also required.

ICI had submitted a dry milling study with PP #2F2624. However, RCB, upon re-reviewing the data, finds this study questionable. RCB notes that permethrin residues on corn grain were reported to be 0.031 ppm in one summary table, as 0.016 ppm on another summary table, as <0.01 ppm in one lab data sheet, and 0.031 ppm on another. Similarly, permethrin residues on treated corn meal were reported as "Trace" on one summary sheet, 0.037 ppm on a second summary sheet, <0.01 ppm on one lab sheet, and 0.109 ppm on a second lab sheet. Depending upon which values are selected, the concentration factor for corn meal, a human food, ranges from <1X to 6.8X. Furthermore, permethrin residues in check samples of crude oil, deodorized oil, and soapstock ranged from 63-64% of the levels reported in treated samples, and the summed residues in check samples of these commodities ranged from 63-76% of the levels reported in treated samples. Chromatograms of treated and untreated oil, reflecting analyses for permethrin, were not submitted with the ICI study, and mass spec was not used to confirm the identity of permethrin. So RCB cannot determine whether substrate interferences were present in untreated oil or if permethrin was present as a contaminant.

The petitioner will need to conduct an adequate dry milling study in order to determine whether residues concentrate in corn meal and oil. At this time, RCB does not know which residue values are correct in the available dry milling study, especially with respect to the corn meal fraction. Raw data sheets and chromatograms should be submitted for validation purposes. The petitioner's data show that residues of permethrin in oil are largely degraded by the deodorizing process (see below), but if all the permethrin concentrates in crude oil (theoretical concentration factor, 25X) as a result of dry milling, residues in oil could still exceed 0.05 ppm, the tolerance on the rac.

The petitioner has submitted a wet milling study and a fortified oil processing study which indicate that residues of permethrin and its metabolites did not concentrate in bleached, refined, deodorized oil derived from wet milling.

permethrin residues did not concentrate in crude oil from the wet milling process, as opposed to the concentration into crude oil reported in the dry milling study. When crude oil was spiked with permethrin (0.22 ppm), permethrin residues in the deodorized oil were only 0.01 ppm; it seems that permethrin is largely removed by the deodorizing process. The check samples of all fractions from the FMC study were reported as non-detectable, with the exception of DCVA residues in crude oil (0.05 ppm) and refined oil (0.01 ppm).

In the ICI study, the permethrin residue level in crude oil was reported as 0.19 ppm. In the FMC study, the crude oil had been spiked at a level of 0.22 ppm before refining and deodorizing. Therefore both studies should have had the same end result, namely, a permethrin residue level of about 0.01 ppm in the deodorized oil. The ICI study reported 0.14 ppm permethrin in deodorized oil. There are two possible explanations for the divergent results:

1) The peak attributed to permethrin in the ICI study actually represents an interference, or

2) The deodorizing processes were different.

Neither ICI nor FMC provided details on the deodorizing process. Details of the oil refining process were supposed to be included in Appendix B of this submission, but descriptions of the bleaching and deodorizing processes were omitted. The petitioner will need to describe the deodorizing process used on the oil so that RCB can determine whether it adequately reflected common commercial practice. If the deodorizing process did reflect common commercial practice, RCB could conclude that deodorizing removes up to 75% of permethrin residues from bleached, refined oil.

Even though the petitioner fortified the grain with DCVA at levels that were below the limit of determination, it is apparent that residues of both DCVA and 3-PBA concentrate in the crude oil. What happens after that is not entirely clear, for the petitioner has not provided residue data on DCVA and 3-PBA in soapstock.

The petitioner will need to furnish residue data reflecting analyses for DCVA and 3-PBA on soapstock. The petitioner believes that DCVA resembles the fatty acids in soapstock and would partition into the aqueous layer containing the soapstock. The petitioner is probably correct. The available data indicate that the DCVA residue level in crude oil was 0.62 ppm and was not detectable in the refined oil; therefore the DCVA must have partitioned into the soapstock (18.5 g). If this is the case, a residue level of 3.0 ppm can be calculated (90/18.5 x 0.62 ppm), or a concentration factor of 43 for soapstock. Because the yield of soapstock (18.5 g) is so small relative to the amount of crude oil used (90 g), it is possible for the residue level of 3-PBA to be higher in soapstock than on the corn grain, even if most of the 3-PBA does partition into the oil.

Although there are not sufficient data to estimate the relative amount of DCVA in the terminal grain residues, data on forage and fodder indicate that DCVA may constitute at least 41% of the terminal residues.

In the absence of residue data reflecting analyses of 2 of the 3 residues of concern (one of which the petitioner himself believes

will concentrate), how can RCB determine whether permethrin and its metabolites concentrate in soapstock?

According to the CRC Handbook of Processing and Utilization in Agriculture (provided by the petitioner), purified corn bran is an ingredient in animal feeds and in high fiber foods. The Corn Refining Association has informed RCB that corn bran is a commodity which is bought and sold and may enter interstate commerce. Therefore the petitioner will also need to submit residue data on corn bran from a wet milling process. Raw data sheets and chromatograms should be submitted for validation purposes.

Meat, Milk, Poultry, and Eggs

Soapstock may constitute up to 5% of the diet of cattle and poultry. At this time RCB cannot determine whether the established tolerances on animal commodities would adequately cover secondary residues expected to arise from the proposed use because the petitioner has provided neither adequate residue data reflecting analyses for DCVA and 3-PBA on soapstock nor residue data on corn bran.

Other Considerations

FMC's originally proposed use allowed 3 applications at a rate of 0.2 lb. a.i./A. When the use was amended to permit application prior to ear formation only, the restriction on the number of applications was dropped from the label, as no residues were expected on corn grain from this early use. Since the establishment of the tolerance on field corn, the label has been amended to permit application prior to the brown silk stage. The petitioner has submitted residue data which indicate that detectable levels of permethrin occasionally can arise from this use. A permethrin residue level of 0.01 ppm was reported from a trial conducted in Ohio, in which an application rate of 3 x 0.2 lb. a.i./A was used and a PHI of 58 days was observed. Finite residues (0.013 ppm) of permethrin were also reported from a field trial conducted in NB by ICI (submitted with PP #2F2624). In this trial an application rate of 3 x 0.2 lb. a.i./A was used, and a PHI of 54 days was observed. Therefore, RCB recommends that the PM inform FMC that the number of applications and the treatment interval should be stipulated on the label. The residue data submitted by FMC and ICI reflect up to 6 applications of 0.2 lb. a.i./A.

The petitioner has not provided residue data for residues of DCVA and 3-PBA on soapstock. It seems likely that residues of DCVA will concentrate in soapstock. If the requested residue data establish that residues of DCVA and/or 3-PBA concentrate in soapstock in excess of 0.05 ppm, the Delaney amendment would prohibit the establishment of a feed additive tolerance. This consideration is also extended to corn bran. Similarly, a food additive tolerance may not be established on corn meal, if residues concentrate in this commodity.

The petitioner should be sent a copy of this review.

Conclusions

1a. RCB has no objection to the use of banded applications or aerial equipment during the preemergent period.

1b. No PHI is stipulated. The petitioner needs to submit a revised Section B/labelin which he specifies the intended PHI, which should be adequately reflected by the residue data.

2. The nature of the residue is adequately understood. In plants the residues of concern are permethrin and the acid, DCVA, and the alcohol, 3-PBA. In addition to these residues, 3-phenoxybenzoic acid is a residue of concern in animals.

3. RCB concludes that adequate analytical methodology was used to determine residues of permethrin in all matrices; adequate methodology was used to determine residues of DCVA and 3-PBA in all matrices except soapstock, for which no methodology was available, according to the petitioner. The petitioner will need to provide adequate methodology for the determination of DCVA and 3-PBA in soapstock.

4. Even though some of the data reflect exaggerated application rates (5 x 0.2 lb. a.i./A), RCB considers the available data to be far too skimpy to support PHI's of less than 45 days. Residue data from 3 trials using the higher rate exhibited residue levels of >0.03 ppm, which approaches the tolerance level (0.05 ppm). In order to support the proposed use on corn, residue data reflecting any intended PHI (whatever it may be) would be required from all wheat growing areas, especially the corn belt. The shortest PHI observed in corn belt field trials was 46 days (IA).

5a. According to the CRC Handbook of Processing and Utilization in Agriculture (provided by the petitioner), purified corn bran is an ingredient in animal feeds and in high fiber foods. The Corn Refining Association has informed RCB that corn bran is a commodity which is bought and sold and may enter interstate commerce. Therefore the petitioner will also need to submit residue data on corn bran from a wet milling process. Raw data sheets and chromatograms should be submitted for validation purposes.

5b. Details of the oil refining process were supposed to be included in Appendix B of this submission, but descriptions of the bleaching and deodorizing procedures were omitted. The petitioner will need to describe the deodorizing process used on the oil so that RCB can determine whether it adequately reflected common commercial practice. If the deodorizing process did reflect common commercial practice, RCB could

conclude that deodorizing removes up to 75% of the permethrin residues from refined, bleached oil.

5c. The petitioner will need to furnish residue data reflecting analyses for DCVA and 3-PBA on soapstock. The petitioner believes that DCVA resembles the fatty acids in soapstock and would partition into the aqueous layer containing the soapstock. In the absence of residue data reflecting analyses of 2 of the 3 residues of concern (one of which the petitioner himself believes will concentrate), RCB cannot determine whether residues concentrate in excess of 0.05 ppm in soapstock.

5d. Since residues of permethrin on corn are expected to arise from the amended use, the petitioner will need to conduct an adequate dry milling study in order to determine whether residues concentrate in corn meal and oil. At this time, there are too many discrepancies in the residue data, especially with respect to corn meal. Raw data sheets and chromatograms should be submitted for validation purposes. The petitioner's data show that residues of permethrin in oil are largely degraded by the deodorizing process, but if all the permethrin concentrates in crude oil (theoretical concentration factor, 25X) as a result of dry milling, residues in oil could still exceed 0.05 ppm, the tolerance on the rac. RCB questions the validity of the dry milling study submitted by ICI with PP #2F2624 because residue levels in check samples of oil and soapstock ranged up to 76% of the levels found in treated samples and because of reporting vagaries; the concentration factor of permethrin in corn meal ranged from <1X to 6.8X, depending upon which of the reported values were used.

6. Soapstock may constitute up to 5% of the diet of cattle and poultry. At this time RCB cannot determine whether the established tolerances on animal commodities would adequately cover secondary residues expected to arise from the proposed use because the petitioner has neither provided adequate residue data reflecting analyses for DCVA and 3-PBA on soapstock nor provided residue data on corn bran.

Recommendations

RCB recommends against the proposed full season use of permethrin on field corn for the reasons outlined in Conclusions 1b, 3, 4, 5a, 5b, 5c, 5d, and 6 cited immediately above. From this date, all correspondence should refer to the unresolved Conclusions as numbered above.

cc: TOX, PMSD/ISB, PM #15, PP #1F2476, R.F., Permethrin S.F., Reviewer - Deyrup, Amended Use File (permethrin or Pounce), Circu, EAB

RDI:JHONley:4/23/87:RDSchmitt:4/24/87
TS-769:RCB:CM#2:RM810:X7484:CDeyrup:cd:4/24/87