

US EPA ARCHIVE DOCUMENT

1-8-93

**MEMORANDUM**

**SUBJECT:** PP#3F2884. Chlorpyrifos in Livestock Commodities.  
Petition to Separate the Metabolite Trichloropyridinol  
(TCP) from the Tolerance Expression. Amendment dated  
11/3/92.

DP Barcode D185093. CBTS # 10941.  
MRID # 425427-01.

**FROM:** Michael T. Flood, Ph.D., Chemist  
Tolerance Petition Section II  
Chemistry Branch I -- Tolerance Support  
Health Effects Division (H7509C)

**THROUGH:** Debra F. Edwards, Ph.D., Chief  
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**TO:** Dennis Edwards, PM 19  
Insecticide-Rodenticide Branch  
Registration Division (H7505C)

**This memorandum is being expedited at the 12/3/92 request of  
Lawrence E. Culleen, Acting Director, Registration Division.  
After consultation with R. Cool of RD, the due date is 1/30/92.**

With letter dated 11/3/92, DowElanco is submitting results  
of a residue transfer study of chlorpyrifos to milk and cream  
from dairy cows wearing chlorpyrifos-impregnated ear tags. A  
revised Section F is also included in which tolerances are  
proposed for racs for which registration or reregistration is  
sought. (These tolerances will be listed later in this memo.)  
We note that a similar chlorpyrifos action is being reviewed  
concurrently by L. Cheng of CBRS.

A tolerance of 0.5 ppm (reflecting 0.02 ppm in whole milk)  
has been established for milkfat under 40 CFR 180.342 for the  
combined residues of chlorpyrifos (O,O-diethyl O-(3,5,6-  
trichloro-2-pyridyl)phosphorothioate and its metabolite 3,5,6-  
trichloro-2-pyridinol (TCP). Because TOX has not expressed  
concern over the TCP metabolite with regard to regulation of  
residues on commodities treated with chlorpyrifos, it is being  
removed from the tolerance expression. Listed tolerances of 2.0  
ppm for the fat, meat and mby of cattle include contributions

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from dermal application. At present only eartag use is permitted, and CBTS concluded that tolerances of 0.2 ppm be established for cattle meat and fat and 0.05 ppm for cattle meat byproducts (L. Rodriguez, memo of 4/18/90). These proposed tolerances include dietary contribution of chlorpyrifos from animal feeds as well as from eartag use. Because residue data reflecting chlorpyrifos in milk from eartag use were lacking, DowElanco has conducted a residue transfer study. A protocol for this study was reviewed in our 3/5/92 memo.

### Conclusions

1. Data from the residue transfer study indicate that residues in whole milk and milk fat resulting from eartag use should not be a significant fraction of the residues resulting from intake of animal feeds containing chlorpyrifos. Therefore the tolerances should be those proposed in the absence of dermal residue data. The tolerance expression should read "Milk fat (reflecting 0.01 ppm in whole milk)....0.25 ppm".
2. The appropriate tolerances for meat and meat byproducts of cattle, goats, hogs and sheep are 0.05 ppm. The appropriate tolerance for the fat of cattle is 0.3 ppm. The appropriate tolerances for the fat of goats, hogs and sheep are 0.2 ppm. DowElanco should submit a revised Section F in which a tolerance of 0.3 ppm is proposed for residues of chlorpyrifos in the fat of cattle. This latter tolerance includes a contribution of 0.1 ppm due to eartag use. (Tolerances for horse meat, fat and meat byproducts can remain at the proposed 0.25 ppm.)

The recommendations made in this memo concerning tolerances for cattle fat and meat supersede those made in CBTS memos dated 5/17/91 and 4/18/90. Refer to discussion in the "Detailed Considerations" section.

3. The remaining proposed tolerances were recommended by CB in three memos with the following exceptions:

Tolerances for sorghum grain, forage, fodder and grain milling fractions; sunflower seeds and hulls; corn, fresh, corn oil and soapstock are not supported by adequate residue data.

### Recommendation

CBTS recommends against the proposed tolerances for reasons given in Conclusions 2 (revised tolerance for cattle fat) and 3 (residue data necessary on sorghum, sunflower seeds, fresh corn

and certain processed commodities).

### Detailed Considerations

DowElanco has submitted the following report:

"Residues of Chlorpyrifos in Milk and Cream from Dairy Cows Wearing Chlorpyrifos-Impregnated Plastic Ear Tags;" C.K. Robb, J.E. Stafford, J.A. Ostrander; 10/23/92; Performing Laboratory: DowElanco, Midland, MI and Bio-Life Associates, Neillsville, WI; Laboratory Study ID RES92025. (MRID # 425427-01)

Insecticide-impregnated eartags were prepared by Y-Text Corporation. Three levels were used in dosing: 0x maximum use rate; 1x maximum use rate (2 eartags/cow, each containing 5% chlorpyrifos); and 5x maximum use rate (4 eartags/cow, each containing 12.5% chlorpyrifos). Three Holstein dairy cows were dosed at each level. Eartags remained attached for 49 days to the 1x cows and to two of the three 0x cows. The tags remained attached for 75 days to the 5x cows and to the remaining 0x cow. Afterwards, the tags were analyzed to determine chlorpyrifos loss.

Duplicate composite 800-mL samples were collected daily from day 1 through day 28 except for day 26 when triplicate samples were collected. Single composite 800-mL samples were collected daily for each cow from day 29 through the end of the study. Samples were held in frozen storage from the time of milking until analysis. The maximum interval between sampling and analysis was 74 days. Chlorpyrifos residues are stable under frozen storage for this time period (Registration Standard, 2/29/84). A storage stability study was conducted on eartags stored at ambient temperature. Chlorpyrifos residues were found to be stable through the duration of the study -- up to 137 days. Not surprisingly, significant weight loss -- typically, greater than 50% -- occurred in ear tags worn during the study.

Residues of chlorpyrifos were determined by slightly modified ACR 90.2. Samples of whole milk, skim milk and cream were heated prior to analysis to aid in mixing. After addition of salt and, in the case of cream, water, the chlorpyrifos was partitioned into acetone. A portion of the acetone was evaporated and the resulting solution partitioned with hexane. The hexane solution was in turn partitioned with acetonitrile, taken to dryness and redissolved in acetone. Dilute phosphoric acid was added, and the sample was purified by C18 SPE using methanol as an eluent. After partitioning into hexane, chlorpyrifos was analyzed by GC using flame photometric detection.

Recoveries of chlorpyrifos from whole milk averaged  $99 \pm 9\%$  ( $n=44$ ) at fortification levels ranging from 0.01 ppm to 0.1 ppm. Recoveries from skim milk averaged  $106 \pm 9\%$  ( $n=8$ ) at levels ranging from 0.01 ppm to 0.05 ppm. Recoveries from cream averaged  $77 \pm 16\%$  ( $n=20$ ) at levels ranging from 0.01 ppm to 0.10 ppm. Chromatograms show well resolved peaks at fortification levels of 0.01  $\mu\text{g/g}$ . (We assume that chromatogram from Sample No. 303665 was a result of fortification of 0.01  $\mu\text{g/g}$  rather than the reported 1.01  $\mu\text{g/g}$ .)

No residues of chlorpyrifos were detected ( $<0.003$  ppm) in whole milk treated at the 0x or 1x rate. This study was concluded after 49 days. The whole milk from one of three cows treated at the 5x rate showed chlorpyrifos residues above 0.003 but below the level of quantitation (0.01 ppm). These residues were present from day 19 through 44 and then declined below the detection limit until the study was terminated at 75 days.

Whole milk from days 26-28 from the 0x and 5x-treated cows was separated into skim milk and cream and analyzed. As expected, no residues were detected in skim milk. Residues of chlorpyrifos found in cream ranged from 0.02-0.04  $\mu\text{g/g}$ . Cream samples from day 28 were analyzed for butterfat by Land O'Lakes, Inc., Greenwood, WI. Percent butterfat ranged from 35.0 to 40.0. Therefore, the maximum residue limit for chlorpyrifos in milkfat as a result of 5x exposure would be  $0.04 \mu\text{g/g} / 0.35 = 0.11 \mu\text{g/g}$ . Although we would not necessarily predict that the expected maximum level in milkfat resulting from 1x exposure would be one-fifth of this number, we can say that the expected maximum residue limit from eartag use would not significantly affect the proposed milkfat tolerance of 0.25 ppm (see discussion below).

#### Section F

DowElanco is proposing the following tolerances as listed in the following tables:

Tolerances for Chlorpyrifos Proposed  
as Revisions to 40 CFR 180.342

Raw Agricultural Commodity	Proposed Tolerance (ppm)
Alfalfa forage	3
Alfalfa hay	13
Bananas, whole	0.1
Bananas, pulp with peel removed	0.01
Bean forage	0.7
Broccoli	1
Brussels sprouts	1
Cabbage	1
Cattle, fat	0.2
Cattle, meat and meat byproducts	0.05
Cauliflower	1
Cherries	1
Chinese cabbage	1
Corn, field, grain	0.05
Corn, fresh (inc. sweet K-CWHR)	0.05
Corn forage and fodder	8
Cottonseed	0.2
Cucumbers	0.05
Eggs	0.01
Figs	0.01
Goats, fat	0.2
Goats, meat and meat byproducts	0.05
Hogs, fat	0.2
Hogs, meat and meat byproducts	0.05

Horses, meat, fat, and meat byproducts	0.25
Legume vegetables, succulent or dried (except soybeans)	0.05
Milk, fat	0.25
Milk, whole	0.01
Mint, hay	0.8
Nectarines	0.01
Peaches	0.01
Pea forage	0.7
Peanut hulls	2
Peanuts	0.2
Pears	0.01
Plums (fresh prunes)	0.01
Poultry, meat, fat, and meat byproducts (inc. turkeys)	0.1
Pumpkins	0.05
Radishes	2
Rutabagas	0.5
Sheep, fat	0.2
Sheep, meat and meat byproducts	0.05
Sorghum fodder	4
Sorghum forage	1
Sorghum grain	0.3
Soybean grain	0.3
Soybean forage	0.7
Strawberries	0.2
Sunflower seeds	0.2
Sweet potatoes	0.05
Turnip greens	0.3
Turnips	1

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The following tolerances are proposed as revisions to 40 CFR 185.1000 (food additive tolerances):

Processed Food Commodity	Proposed Tolerance (ppm)
Corn oil	1.5
Mint oil	8
Peanut oil	0.4

The following tolerances are proposed as revisions to 40 CFR 186.1000 (feed additive tolerances):

Processed Commodity	Tolerance (ppm)
Corn soapstock	0.5
Sorghum, grain, milling fractions	0.8
Sunflower seed hulls	0.4

#### CBTS Comments

Meat and Milk The following tolerances for chlorpyrifos, per se, were determined to be appropriate for meat and milk in the absence of dermal uses (Debra Edwards, memo of 3/21/89):

Fat of cattle	0.2 ppm
Meat and meat byproducts of cattle	0.05 ppm
Milk fat	0.25 ppm
Whole milk	0.01 ppm

Later, after reviewing residue data reflecting use of chlorpyrifos-impregnated eartags, CB concluded that the tolerance for cattle fat should be increased by 0.1 ppm due to eartag uses (L. Rodriguez, memo of 4/18/90). However, the meat tolerances recommended by D. Edwards were listed incorrectly as 0.05 ppm for fat and 0.2 ppm for meat. Therefore, the tolerance proposed to include eartag use was 0.2 ppm for cattle fat. This error was carried over into our 5/17/91 memo (M. Flood) which also requested tolerances of 0.2 ppm for cattle meat and cattle fat and 0.05 ppm for meat byproducts. The appropriate tolerances, which include a contribution due to eartag use, should be 0.05 ppm for chlorpyrifos residues in meat and meat byproducts and 0.3 ppm for chlorpyrifos residues in the fat of cattle.

Appropriate tolerances for chlorpyrifos in the fat of goats, hogs and sheep are 0.2 ppm; appropriate tolerances for the meat

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and meat byproducts of these animals are 0.05 ppm. Tolerances for chlorpyrifos in fat, meat and meat byproducts of horses may remain at 0.25 ppm, as proposed. These higher tolerances are the result of higher estimated chlorpyrifos dietary levels (K. Arne, memo of 9/8/83).

As concluded above, residues in milk and milkfat due to combined ingestion of chlorpyrifos from animal feeds and eartag use should not exceed the tolerances proposed from use solely in/on rags intended as animal feed items. The tolerance expression should read "Milk fat (reflecting 0.01 ppm in whole milk).....0.25 ppm".

The remaining tolerances were considered appropriate by CB in memos dated 12/15/88, 1/13/89 (Debra Edwards) and 12/21/88 (Stephanie Willett) with the following exceptions: tolerances for sorghum grain, forage and fodder and grain milling fractions; sunflower seeds and hulls; corn, fresh, corn oil and soapstock were not supported by CB because of outstanding data gaps identified in the Second Round Review (SRR) (10/14/88). Since the SRR was issued, DowElanco submitted data for sweet corn, sorghum, sunflowers and snap beans; but CBRS has required additional residue data (L. Cheng, memo of 5/19/92).

cc: Circ., RF, Reg.Std.File, Mike Flood, E. Haeberer, PP#3F2884, L. Cheng (CBRS), J. Kariya (H7509C).

H7509C:CBTS:Reviewer(MTF):CM#2:Rm804P:305-6362:typist(mtf):1/8/93.  
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