MEMORANDUM

Subject: PP#2F2628: Pendimethalin in Sweet Corn. Evaluation of residue data and analytical method.

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Thru: Charles L. Trichilo, Chief
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To: Robert J. Taylor (PM#25)
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and

Toxicology Branch
Hazard Evaluation Division (TS-769)

The American Cyanamid Company proposes tolerances for combined residues of the herbicide pendimethalin, N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine, and its metabolite 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol at 0.1 ppm in or on sweet corn grain, sweet corn forage, and sweet corn fodder.

A temporary tolerance for residues of pendimethalin in sweet corn has been established (PP#1G2511) at 0.1 ppm and is to expire April 1, 1983.

Permanent tolerances have been established ($180.361) on several commodities (field corn, cottonseed, peanuts, rice, soybeans, sunflower seeds) at levels of 0.05-0.25 ppm.
Conclusions

1. The nature of the residue in plants and animals is adequately understood. The parent compound pendimethalin and its benzyl alcohol metabolite are the significant components of the residues.
2. Adequate analytical methods are available for enforcement purposes.

3(a). Residues of pendimethalin in sweet corn grain or forage and fodder are not likely to exceed the proposed tolerance. The tolerance level actually represents the method's sensitivities for pendimethalin and its metabolites.

3(b). Residues of atrazine or Bladex are not likely to exceed the established tolerances from the proposed tank-mix uses.

4. No resides are likely to result in eggs, milk, meat, fat, or meat byproducts of cattle, goats, hogs, horses, poultry, and sheep [§180.6(a)(3)].

Recommendation

TOX and EFB considerations permitting, we recommend for the proposed tolerances.
Detailed Considerations

Proposed Use

Pendimethalin is formulated as PROWL®, an emulsifiable concentrate containing 4 lb. active ingredient per gallon. The formulation is to be used alone or in tank-mix combinations with the herbicides *Bladex or *atrazine as a preemergence or postemergence application in sweet corn (processing varieties only) in Wisconsin and Minnesota only.

Pendimethalin alone

Apply preemergence after planting, air or ground application, at broadcast rates of 0.75-2 lb. act/A depending upon the soil type. Band applications are permitted at proportionate rates.

Pendimethalin plus atrazine, or Bladex

Air or ground, preemergent or early postemergent (no later than 2-leaf stage of corn), at rates of 0.75-1.5 lb. pendimethalin + 1.0-1.6 lb. atrazine or 1.0-2.4 lb. cyanazine per acre.

*Bladex (cyanazine), 2-[[4-chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methylpropionitrile, is registered for use on sweet corn at preplant rate of 4 lb. act/A and postemergence rate of 2 lb. act/A. Tolerances are established on sweet corn grain at 0.5 ppm and forage and fodder at 0.2 ppm.

*Atrazine (AAtrex), 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, is registered for use on sweet corn at preplant rate of 4 lb. act/A and postemergence rate of 4 lb. act/A. Grazing or feeding of treated areas for 21 days after treatment is not permitted. Tolerances are established at 0.25 ppm on sweet corn grain and 15 ppm on forage and fodder.
The manufacturing process for technical pendimethalin is included in PP#5F1556. Technical pendimethalin contains 91-94% pendimethalin. The tech. pendimethalin also contains an N-nitroso component. Data were submitted in PP#1G2511 which show that the N-nitroso component in batches of Prowl is less than [redacted] ppm. A study with the radiolabelled N-nitroso component showed no detectable residues (less than one part per billion) on soybeans treated at a rate equivalent to about 100 times the soil concentration resulting from a 1.5 lb. pendimethalin application rate. It is therefore unlikely that the N-nitroso component will present a residue problem in sweet corn.

The formulation's inert ingredients are cleared for use under $180.1001.

Nature of the Residue

We have considered the plant and animal metabolism of pendimethalin in previous reviews (cf. PP#0F2401). Pendimethalin is absorbed, metabolized, and translocated by rice, beans, potatoes, corn, cotton, and peanut plants. The significant components in plant residues are the parent compound and its benzyl alcohol metabolite.

Feeding studies with animals show that ingested pendimethalin is extensively metabolized and excreted by cows, goats, and rats. Some deposition of residues occurs in tissues, but no tendency towards storage or concentration is noted.

The nature of the residue in plants and animals is adequately understood.

Analytical Methods

A sample is extracted by blending with a methanol/chloroform solvent and filtered. For the parent, an aliquot of the filtrate is evaporated to dryness, and the residue is taken up with hexane. The hexane extract is cleaned up on a florisil column and eluted with a mixture of benzene and hexane. The eluate is evaporated to dryness, and the residue is taken up with benzene and determined by gas chromatography using an electron capture detection system (ECGC).
The metabolite is initially extracted with an acidic methanol solution and filtered. An aliquot of the filtrate is treated with an acetic anhydride solution which forms an acetyl derivative. The acetylated residue is extracted into hexane and evaporated to dryness. The residue is cleaned up on a florisil column and determined as above.

Untreated (control) samples had <0.02 ppm equivalent residues of pendimethalin and its metabolite. Control samples were fortified with pendimethalin and its metabolite at levels of 0.05-1.0 ppm. Recoveries were 75-127%.

The method's sensitivity is reported to be about 0.05 ppm.

The methods have been successfully tested on cottonseed at levels of 0.05 ppm and 0.1 ppm (PP#5F1556).

We believe the results of the method trials can be extended to include sweet corn.

Adequate analytical methods are available for enforcement purposes.

Methods for atrazine and Bladex are included in the Pesticide Analytical Manual, Volume II. The method for atrazine involves a more specific residue determination by gas chromatography. Both the ultraviolet and gas chromatography procedures for atrazine are also included in the work of Mattson, et. al., J. Ag. & Pd. Chem., 13, 120(1965).

Residue Data

Sweet corn samples were obtained from crops grown in representative areas of the U.S. (including Wisconsin and Minnesota) in soils treated as proposed with pendimethalin alone or in tank-mix combinations. No residues of pendimethalin (<0.05 ppm) or its metabolite (<0.05 ppm) were noted in corn grain at 57-116 days after treatment; in silage at 37-116 days; and, in forage, fodder, and stover at 70-102 days following treatments. The treatments entailed applications of pendimethalin alone at rates of 1.5-4.0 lb. act/A (2X maximum proposed) or, in tank-mix combinations of 1.5-2.4 lb. atrazine/A or 0.4-2.5 lb. Bladex/A.
No detectable residues (<0.05 ppm) of atrazine or Bladex were found in corn grain, silage, forage or fodder from any uses.

We conclude that residues of pendimethalin or its metabolite, if any, in sweet corn grain or sweet corn forage and fodder are not likely to exceed the proposed tolerance of 0.1 ppm.

Residues of atrazine ($180.220) or Bladex($180.307) are not likely to exceed the established tolerances from the proposed tank-mix uses.

The pendimethalin tolerance actually represents the residue method's sensitivities for pendimethalin and its metabolite. Real residues, if any, would be much less than 0.05 ppm.

**Meat, Milk, and Eggs**

Livestock feeding studies were submitted in PP#5F1556. Lactating cows and lactating goats were fed pendimethalin daily at dietary levels of 0.5, 1.5, and 20 ppm for periods of 10-21 days. No residues were noted in the milk of cows or goats due to feeding levels of 0.5-1.5 ppm.

Tissue analyses were performed only on the goats. Low levels of total radioactivity were noted. The liver had activity equivalent to 0.03 ppm, 0.04 ppm, and 0.25 ppm corresponding to the 0.5, 1.5, and 20 ppm feeding levels. The kidney had respective residue levels of 0.01, 0.04 and 0.09 ppm. The fat had residue levels of 0.01 ppm, 0.01 ppm, and 0.03 ppm from respective feeding levels of 0.5, 1.5, and 20 ppm. All other tissues had no detectable radioactivity (<0.01 ppm, method detection limit) from all feeding levels. Characterization of the urine and feces showed pendimethalin to be extensively metabolized and rapidly excreted. It is therefore probable that pendimethalin and its metabolite represent only a small portion of the total radioactivity noted in some tissues.

Sweet corn forage and fodder and sweet corn cannery waste are used as feed for cattle, sheep, and goats at levels of 30-50% of the daily diets. Based upon the proposed tolerance level (0.1 ppm), estimates of the maximum levels of residues likely to be ingested are as follows: cattle (0.05 ppm); goats and sheep (0.05 ppm).
However, these estimates are exaggerated since real residues, if any, are likely to be considerably less than the proposed 0.1 ppm. As a result, no residues of pendimethalin or its metabolite are likely to result in eggs, milk, meat, fat, and meat byproducts of livestock [§180.6(a)(3)].

cc: RF, Circu., Reviewer, Thompson, FDA, TOX, EFB, EEB,
PP#2F2628
RDI: Quick, 7/9/82; Schmitt, 7/12/82
CHEMICAL: PROWL

CCPR NO.: None

Codex Status:

[ ] No Codex Proposal

Step 6 or above

Proposed U. S. Tolerances:

N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine and its metabolite 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzyl) alcohol

Residue (if Step 9):

Crop(s) Limit (mg/kg)

Crop(s) Tol. (ppm)

Sweet corn grain 0.1 ppm
Sweet corn fodder 0.1 ppm
Sweet corn forage 0.1 ppm

CANADIAN LIMIT

Residue:

Crop Limit (ppm)

None

MEXICAN TOLERANCIA

Residue:

Crop Tolerancia (ppm)

None

Notes: